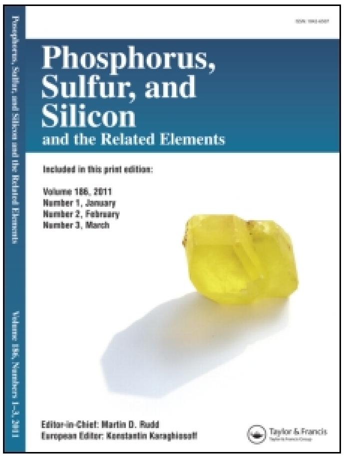

**Phosphorus, Sulfur, and Silicon and the Related Elements**
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# REACTIONS OF AMMONIUM SULFIDE AND AND ITS DERIVATIVES. SYNTHESIS OF 4-CHLORO-3,5-DINITROBENZOTRIFLUORIDE 1,6-DINITRO-3,8-BIS(TRIFLUOROMETHYL)-PHENOTHIAZINE, 2,2-DIMETHYL-5-TRIFLUOROMETHYL-7-NITROBENZOTHIAZOLINE AND RELATED COMPOUNDS

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**To cite this Article** Chen, Mei-Jin , Chi, Ching-Sung and Chen, Qing-Yun(1990) 'REACTIONS OF AMMONIUM SULFIDE AND AND ITS DERIVATIVES. SYNTHESIS OF 4-CHLORO-3,5-DINITROBENZOTRIFLUORIDE 1,6-DINITRO-3,8-BIS(TRIFLUOROMETHYL)-PHENOTHIAZINE, 2,2-DIMETHYL-5-TRIFLUOROMETHYL-7-NITROBENZOTHIAZOLINE AND RELATED COMPOUNDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 48: 1, 173 — 180

**To link to this Article: DOI:** 10.1080/10426509008045895

**URL:** http://dx.doi.org/10.1080/10426509008045895

*Phosphorus, Sulfur, and Silicon,* 1990, Vol. 48, pp. 173–180

# REACTIONS OF AMMONIUM SULFIDE AND 4-CHLORO-3,5-DINITROBENZOTRIFLUORIDE AND ITS DERIVATIVES. SYNTHESIS OF 1,6-DINITRO-3,8-BIS(TRIFLUOROMETHYL)-PHENOTHIAZINE, 2,2-DIMETHYL-5-TRIFLUOROMETHYL-7-NITROBENZOTHIAZOLINE AND RELATED COMPOUNDS

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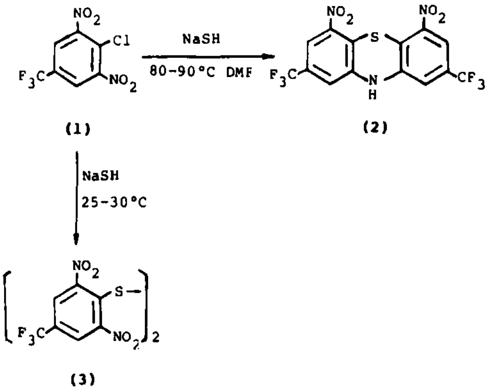
*(Received September 26, 1989; in final form October 3, 1989)*

The reactions of ammonium sulfide and 4-chloro-3.5-dinitrobenzotrifluoride (**1**) in 1,4-dioxane-$H_2O$ system at room temperature in presence and absence of acetone resulted in titled compounds 1,6-dinitro-3,8-bis(trifluoromethyl)phenothiazine (**4**) and 2,2-dimethyl-7-nitrobenzothiazoline (**5**) respectively. With the existence of acetone, compounds 1,2-bis (2′6′-dinitro-4′-trifluoromethylphenylthio)ethane (**6**), 3-oxa-1,5-bis(2′,6′-dinitro-4′-trifluoromethylphenzothia)pentane (**8a**) and 3-oxa-1,5-bis(2′,6′-dinitro-4′-trifluoromethylphenyl)pentane (**8b**) were converted to 5-nitro-7-trifluoromethyl-1,4-benzodithiane (**7**) and 2,2-dimethyl-4-nitro-6-trifluoromethylbenzoimidazoline (**9**), in addition to (**5**). Acetone participated in the cyclization. Under similar conditions, N,N′-bis(2,6-dinitro-4-trifluoromethylphenyl) piperazine (**10**) and N,N′-bis(2′6′-dinitro-4′-trifluoromethylphenyl)-4,7,-10-trioxa-1,13-tridecadiamine (**12**) gave usual corresponding products N,N′-bis(2′-hydroxyamino-6′-nitro-4′-trifluoromethyl-phenyl)piperazine (**11**) and N,N′-bis(2′-amino-6′-nitro-4′-trifluoromethylphenyl)-4,7,10-trioxa-1,13-tridecadiamine (**13**). Single crystal (**5**) is monoclinic, space group C2/c, with $Z = 8$ and unit-cell constants $a = 20.049(16)$, $b = 14.113(8)$, $c = 8.399(3)$ Å, and $\beta = 103.44(5)°$. Based on nmr, ir, elemental analysis and ms, these structures are determined, and possible mechanisms are discussed.

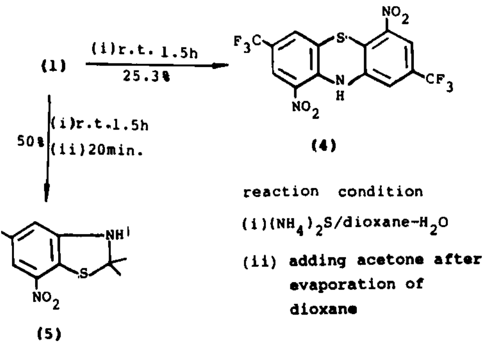
*Key words:* Ammonium sulfide; reduction; nucleophilic substitution; phenothiazine; benzothiazoline; single crystal.

Reduction of nitro groups by $S^{2-}$ or $HS^-$ to amines is classical.[1] However, when activated aromatic nitro compounds, such as 4-chloro-3,5-dinitrobenzotrifluoride (**1**) were used, nucleophilic substitution reactions were usually observed.[2,3] For example, D'Amico *et al.*[2] reported that the reaction of (**1**) with NaSH in DMF at 80–90°C gave compound (**2**), but at 25–30°C none of (**2**) was formed, and a major product (**3**) was isolated. During the course of work relating to the reduction of aromatic nitro compounds, we isolated some unexpected products. Here, we wish to report these results.

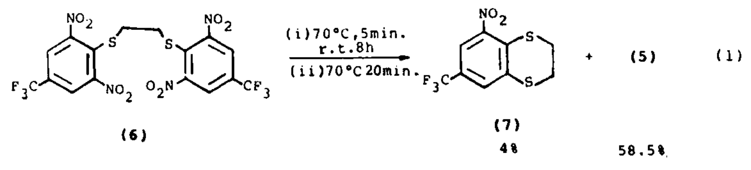
The reaction of $(NH_4)_2S$ with substrate (**1**) in 1,4-dioxane-$H_2O$ (reaction condition (i)) at room temperature gave substituted phenothiazine (**4**) in 25.3% yield, while in the presence of acetone (reaction condition (ii)) (Scheme 1) substituted benzothiazoline (**5**) was obtained in 50% yield. $(NH_4)_2S$ was used both as a nucleophile to replace chlorine atom and as a reducing reagent to

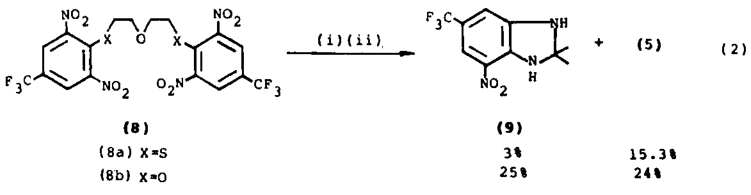


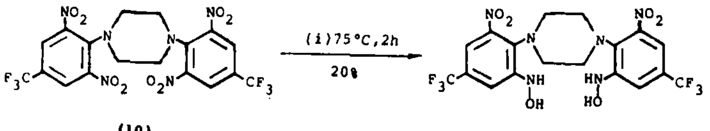
reduce the nitro group. When substrate (**6**) was treated in (i) system, and acetone was then added, compound (**5**) was obtained as the predominate product with 4% of (**7**). Interestingly, similar behaviour towards compound (**8a**) or (**8b**) afforded not only product (**5**), but a five-membered heterocycle, 2,2-dimethyl-4-nitro-6-trifluoromethylbenzoimidazoline (**9**), where acetone was used as a component of the eluant for column chromatography. Apparently, acetone participated in the cyclization of heterocycles (**5**) and (**9**) (Equations 1 and 2). Unlike of the above substrates, even if acetone was present, two compounds (**10**) and (**12**) yielded



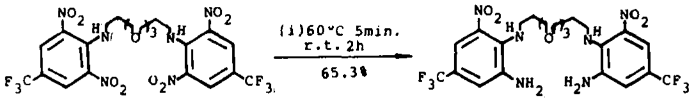
Scheme 1







(10) (11) (3)



(12) (13) (4)

usual products,[1] dihydroxyamine (**11**) and diamine (**13**) respectively as depicted in equation 3, 4 and Table I.

The entire elemental analyses, nmr, ir and mass spectral data are consistent with the proposed structures. The mass spectrum of (**4**) gave the peak of molecular ion at 425 (100%). The ir spectrum showed NH absorption band at 3300 $cm^{-1}$. Two signals of equal integration at $-12.6$ and $-13.3$ ppm in $^{19}F$ NMR, four aromatic protons at 7.72, 7.80, 8.05 and 8.18 ppm in 200 MHz $^{1}H$ NMR clearly demonstrate (**4**) is an asymmetrical structure. (**2**) could be a doubtful structure. The X-ray single crystal analysis convincingly confirmed structure (**5**). The bond distances and angles are listed in Table II and the view of the ORTEP is showed in Figure 1.

Compounds (**8a**) and (**12**), like (**6**), (**8b**) and (**10**), were synthesized from (**1**) and bidentates.[4] With the isolation of (**8a**), (**14**) was collected as a by-product in

TABLE I

Reactions of ammonium sulfide and nitro compounds

| Substrates | Solvent | Temperature(°C) | Time | Product(s)<br>(Yield(%)) |
|---|---|---|---|---|
| **1** | dioxane-$H_2O$ | r.t. | 1.5 h | **4**<br>(25.3) |
| **1** | dioxane-$H_2O$ | r.t. | 1.5 h | **5** |
| | acetone | 70 | 20 min | (50) |
| **6** | dioxane-$H_2O$ | 70(5 min.), r.t. | (8h) | **5** + **7** |
| | acetone | 70 | 20 min | (58.5) (4) |
| **8a** | dioxane-$H_2O$ | 70–80 | 1 h | **5** + **9** |
| | acetone | 70 | 20 min | (15.3) (3) |
| **8b** | dioxane-$H_2O$ | 80 | 2.5 h | **5** + **9** |
| | acetone | (for chromatography) | | (24) (25) |
| **10** | dioxane-$H_2O$ | 75 | 2 h | **11**<br>(20) |
| **12** | dioxane-$H_2O$ | 60(5 min.), r.t. | (2h) | **13**<br>(65.3) |

TABLE II

Bond distances (Å) and angles (°) for $C_{10}H_9N_2F_3O_2S$ (**5**)[a,b]

| | | | | | |
|---|---|---|---|---|---|
| F1-C10 | 1.295(8) | C4-C5 | 1.381(10) | C5-N1 | 1.355(8) |
| F2-C10 | 1.240(11) | C5-C6 | 1.397(10) | S-C7 | 1.842(6) |
| F3-C10 | 1.292(10) | C1-C6 | 1.374(8) | N1-C7 | 1.433(10) |
| C10-C3 | 1.450(10) | O1-N2 | 1.210(6) | C7-C8 | 1.493(10) |
| C1-C2 | 1.365(10) | O2-N2 | 1.210(8) | C7-C9 | 1.473(11) |
| C2-C3 | 1.365(10) | N2-C1 | 1.449(9) | | |
| C3-C4 | 1.379(9) | C6-S | 1.717(6) | | |
| C6-C1-C2 | 122.2 | O1-N2-O2 | 123.5 | C6-C5-N1 | 113.7 |
| C1-C2-C3 | 119.2 | O1-N2-C1 | 117.7 | C5-N1-C7 | 116.6 |
| C2-C3-C4 | 120.8 | O2-N2-C1 | 118.8 | C6-S-C7 | 92.7 |
| C3-C4-C5 | 119.5 | N2-C1-C6 | 118.8 | N1-C7-S | 103.7 |
| C4-C5-C6 | 120.2 | C1-C6-S | 130.8 | | |
| C5-C6-C1 | 118.0 | S-C6-C5 | 111.2 | | |

[a] symmetry operation: $x$, $-y$, $0.5 + z$.

[b] The standard deviation in the last digit is in parentheses.

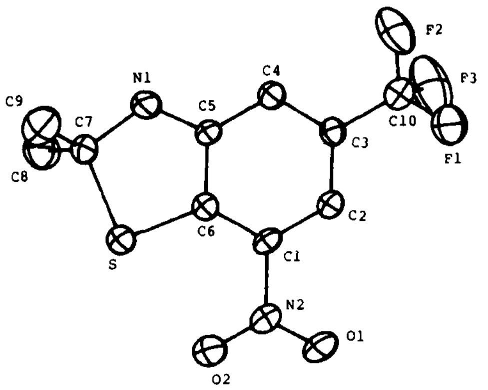
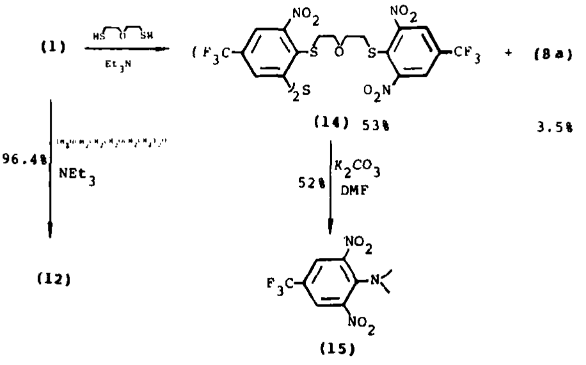
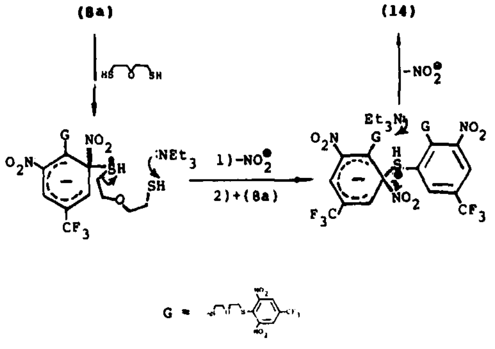


FIGURE 1 ORTEP diagram for (**5**) and labeling scheme.

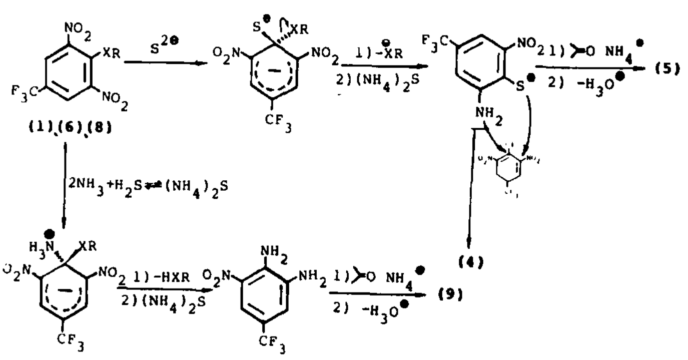


Scheme 2



Scheme 3

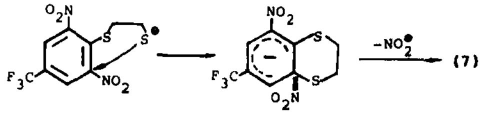
3.5% yield (see Scheme 2). It may be produced by two successive replacements of mercapto group for nitro$^{5}$ on two (**8a**) molecules, and in $K_2CO_3$/DMF, a nucleophilic substitution of it by dimethylamine from the decomposition of DMF resulted in compound (**15**) as shown in Scheme 3.



Scheme 4

The suggested mechanism for the formation of products (**4**), (**5**) and (**9**) is represented in Scheme 4. Probably, the more activated carbon ends para- to $CF_3$ in substrates meet with nucleophilic attack$^{4,6}$ of $S^{2-}$ or $NH_3$ from hydrolysis of $(NH_4)_2S$ to form Meisenheimer complexes.$^{5b,7,8}$ Then, excess of ammonium sulfide makes the nitro groups reduced to produce the precursors of (**4**), (**5**) and (**9**).$^{9}$ Otherwise, uncyclization of two primary amino groups in (**13**) by acetone would be due to the long N-substituted chain. Derived from the departing group $^{-}$XR in Scheme 4, product (**7**) could be yielded by sulfur atom substituting for nitro group$^{5b,7}$ as depicted in equation 5.

A reason that substrates (**10**) and (**12**) did not suffer nucleophilic attack of ammonium sulfide to provide for replaced products is probably due to the lowered reactivities of the carbon ends para- to $CF_3$ caused by the electron-donating N-substituted groups and reduction of nitro groups becomes favourable.



(5)

## EXPERIMENTAL

Melting points were taken in open capillaries and are uncorrected. Infrared spectra were measured on Shimadzu IR-440 spectrophotometer, KCl pellets. $^1$H and $^{19}$F NMR spectra were performed on a Varian XL-200 and EL-360L spectrometers using $SiMe_4$ as internal standard for $^1$H and $CF_3CO_2H$ as external reference for $^{19}$F. $^{13}$C NMR spectrum was recorded on a FX-90Q spectrometer (90 MHz). High-resolution mass spectra and MS were obtained on Finnigan MAT 8430, and Finnigan-402 spectrometers respectively. All chemical shifts are reported in ppm and wave numbers in $cm^{-1}$.

X-Ray crystallography. 2,2-Dimethyl-5-trifluoromethyl-7-nitrobenzothiazoline (**5**). (a) Crystal data. $C_{10}H_9N_2F_3O_2S$, Mr = 278.25, a = 20.049(16), b = 14.113(8), c = 8.399(3) Å, $\beta$ = 103.44(5)°, U = 2311(2) Å$^3$, monoclinic, space group C2/c, Z = 8, Mo–K$\alpha$ radiation ($\lambda$ = 0.71069 Å), F(000) = 1136.00, $\mu = 2.61\ cm^{-1}$.

(b) Data collection and processing. The intensity data were measured on a Nicolet $R_3$ four circle diffractometer using Mo–K$\alpha$ radiation and $\omega$ scanning. Of the 1708 data collected with $2\theta$ max = 50°, 959 had $F > 5\sigma(F)$, where $\sigma$ is the standard deviation of the background count based on counting statistics, and was used in structure solution and refinement.

(c) Structure solution and refinement. The positions of the nonhydrogen atoms were determined by direct methods (SHELX86) and that of hydrogen atom at NH was obtained by difference maps of electron intensity. The position of other hydrogens were determined by theoretical calculation. At convergence, the discrepancy factors R and R$\omega$ were 0.066 and 0.067 respectively, where $\omega = (\sigma^2(F) = 0.000362F^2)^{-1}$.

Known compounds (**6**), (**7**), (**8b**) and (**10**) were reported in literature.[4]

*1,6-dinitro-3,8-bis(trifluoromethyl)-phenothiazine* (**4**) Into 30 ml 1,4-dioxane containing 5.40 g (20 mmole) 3,5-dinitro-4-chlorobenzotrifluoride (**1**), 24 g solution of $(NH_4)_2S$(S, 8%) was added with stirring and an immediate red colour was observed. After stirring for 1.5 h at room temperature, the solvent was evaporated and the residue was treated with saturated aqueous solution of NaCl and extracted with ethyl acetate. The combined extracts were dried over $Na_2SO_4$. After the evaporation of the solvent, column chromatography on silica gel with petroleum ether–ethyl acetate (3:1, $v/v$) as eluant was performed to give a red product (**4**), 1.25 g, 25.3% yield. m.p. 229–230°C. IR: 1120(m, C-F), 3300(w, NH); NMR: $\delta^1$H(acetone-$d_6$): 7.72(s, 1H, 4-H), 7.80(s, 1H, 9-H), 8.05(s, 1H, 2-H), 8.18(s, 1H, 7-H). $\delta^{19}$F(acetone-$d_6$): −12.6(s, 3F), −13.3(s, 3F); MS: 426(M$^+$ + 1), 425(M$^+$); Anal. Calcd for $C_{14}H_5N_3F_6O_4S$: C, 39.53; H, 1.18; N, 9.88; F, 26.82; S, 7.53; Found: C, 38.67; H, 0.97; N, 9.88; F, 27.35; S, 8.08.

*2,2-dimethyl-5-trifluoromethyl-7-nitrobenzothiazoline* (**5**) Starting materials were mixed as mentioned above. After stirring at r.t. for 1.5 h and evaporating of the solvent at reduced pressure, about 30 ml acetone was added to it, and sulfur powder was filtered off. The filtrate was distallized with a rotary evaporator in 20 min. (70°C) giving a solid. Then, water was allowed to add and extraction with several portions of ethyl acetate was proceeded. After dryness ($Na_2SO_4$) and evaporation, a rapid chromatography (ethyl acetate-petroleum ether, 1:4) was made to remove sulfur and to give a red product (**5**) 2.76 g, 50% yield. m.p. 211.4–211.5°C. IR: 1140(s, C-F), 1170(s, C-N), 1320(s, $NO_2$), 3300(m, NH); NMR: $\delta^1$H(acetone-$d_6$): 1.76(s, 6H, $CH_3$), 6.35(s, 1H, ArH, para- to $NO_2$), 7.10(s, 1H, ArH, ortho- to $NO_2$), 3.15(s, 1H, NH). $\delta^{19}$F(acetone-$d_6$): −14.0; MS: 278(M$^+$), 263(M$^+$-$CH_3$), 217(263 − $NO_2$); Anal. Calcd for $C_{10}H_9N_2F_3O_2S$: C, 43.17; H, 3.24; N, 10.07; F, 20.50; S, 11.51; Found: C; 43.20; H, 3.19; N, 10.27; F, 20.65; S, 11.68.

*3-oxa-1,5-bis(2′,6′-dinitro-4′-trifluoromethylphenzothia)pentane* (**8a**)

*bis{3-nitro-4-trifluoromethyl-2-[3′-oxa-5′-(2″,6″-dinitro-4″-trifluoromethylphenylthio]} sulfide* (**14**)

Into 80 ml ethanol containing 27 g (0.1 mole)(**1**) and 11.1 g (0.11 mole) triethylamine, a solution of 7.0 g (0.05 mole)di(2-mercaptoethyl) ether dissolved in 25 ml ethanol was added dropwise with a stirring over a period of 1 h. The temperature was gently raised to 60°C. The mixture was continuously stirred at that temperature for 3 h, and at room temperature for another 3h. The mixture was then poured into water, extracted with ethyl acetate, and dried over $Na_2SO_4$. After evaporation of solvent, 13.9 g yellow solid (**8a**) was obtained. The mother liquor was sustained column chromatography (silica gel) with petroleum ether and acetone (6:4) to give 1 g pale yellow solid (**14**) (3.5% yield) and further (**8a**) 2.5 g (53% yield).

(**8a**), m.p. 95–96°C. IR: 1120(s, C-F), 1150(s, C-S), 1310(s, C-O), 1350(s, sym. $NO_2$); NMR: $\delta^1$H(acetone-$d_6$): 3.03(4H, t, $SCH_2$), 3.53(4H, t, $OCH_2$), 8.43(4H, s, ArH). $\delta^{19}$F(acetone-$d_6$): −14.0; MS: 606(M$^+$), 267($C_7H_2N_2F_3O_2S^+$); Anal. Calcd for $C_{18}H_{12}N_4F_6O_9S_2$: C, 35.64; H, 1.98; N, 9.24; F, 18.81; S, 10.56; Found: C, 35.52; H, 1.81; N, 9.29; F, 18.97; S, 10.81.

**(14)**, m.p. 99–100°C. IR: 1120(s, C-F), 1320(s, C-O), 1550(s, asym. $NO_2$); NMR: $\delta^1H$(acetone-$d_6$): 2.82(8H, m, $SCH_2$),3.32(8H, m, $OCH_2$), 7.45(2H, s, ArH, ortho- to S), 8.20(6H, s, ArH, between $CF_3$ and $NO_2$). $\delta^{19}F$(acetone-$d_6$): −13.0; MS: 582($C_{18}H_{12}N_3F_6O_7S_3^+$), 295($C_9H_6N_2F_3O_4S^+$), 267($C_7H_2N_2F_3O_4S^+$); Anal. Calcd for $C_{36}H_{24}N_6F_{12}O_{14}S_5$: C, 37.50; H, 2.08; N, 7.29; F, 19.79; S, 13.89; Found: C, 37.50; H, 2.01; N, 7.28; F, 18.58; S, 13.89.

*2,2-dimethyl-4-nitro-6-trifluoromethylbenzoimidazoline* **(9)** 1.1 g (1.92 mmole) **(8b)** and 4.6 g ammonium sulfide (S, 8%) were added to 15 ml 1,4-dioxane and 5 ml water. The reaction mixture was allowed to stir in 80°C for 2.5 h. Then, water was poured into the flask, and extraction with ethyl acetate was carried out. After the evaporation of solvent, sulfur powder was mostly filtered off. The filtrate was subjected to a rapid chromatography (ethyl acetate) to remove trace sulfur. Separation by chromatography (silica gel) with toluene-petroleum ether (1:1) and toluene-acetone (4:1) as eluant afforded two red products 0.25 g **(5)** (24% yield) and 0.25 g **(9)** (25% yield).

The procedure for the conversion of **(8a)** to **(5)** and **(9)** is similar to that mentioned above. 6.06 g (10 mmol) **(8a)** and 24 g ammonium sulfide were used. The reaction time was 1 h at 70–80°C, and acetone was used to remove sulfur powder. The filtrate was distillized at 70°C for 20 min. Then acetone-petroleum ether (2:8) was employed as eluant for column separation. 0.41 g **(5)** (15.3% yield) and 0.15 g **(9)** (3% yield) were obtained.

**(9)**, m.p. 182–183°C. IR: 1110(s, C-F), 1540(s, asym. $NO_2$), 3350, 3450(m, NH); NMR: $\delta^1H$(acetone-$d_6$): 1.3(s, 6H, $3CH_3$), 6.1(s, 1H, ArH, para- to $NO_2$), 7.1(s, 1H, ArH, ortho- to $NO_2$). $\delta^{19}F$(acetone-$d_6$): −14.6; MS: 263($M^+ + 2$), 260($M^+ - 1$), 248($M^+ + 2 - CH_3$), 230($M^+ - 1 - 2CH_3$); Anal. Calcd for $C_{10}H_{10}N_3F_3O_2$: C, 45.98; H, 3.83; N, 16.09; F, 21.84: Found: C, 45.63; H, 3.55; N, 15.77; F, 22.13.

*N,N′-bis(2-hydroxyamino-6-nitro-4-trifluoromethylphenyl)-piperazine* **(11)** 1.36 g (2.45 mmole) **(10)**, 5.89 g ammonium sulfide, 20 ml dioxane and 20 ml water were stirred at 75°C for 2 h. After adding of acetone, 0.24 g sulfur powder was filtered off and the filtrate was concentrated. Then the residue was extracted with ethyl acetate. Column chromatography (petroleum ether-ethyl acetate, 4:1, as eluant) gave 250 mg yellow product **(11)**, 20% yield. m.p. 196.0–196.5°C. IR: 1198.0(s, C-F), 1351.0(s, $NO_2$), 3140.0(m, NH), 3472.0(m, OH); NMR: $\delta^1H$(acetone-$d_6$): 0.9(2H, s, NH), 1.3(2H, s, OH), 3.2(8H, s, $CH_2$), 7.5(2H, s, ArH, ortho- to NH-OH), 7.7(2H, s, ArH, ortho- to $NO_2$). $\delta^{19}F$(acetone-$d_6$): −14.0; MS: 526($M^+$), 525($M^+ - 1$). HRMS for $C_{18}H_{16}N_6F_6O_6$: 526.1069, Calcd. 526.0983; Anal. Calcd C, 41.06; H, 3.04; N, 15.97; Found: C, 42.20; H, 3.13; N, 15.86.

*N,N′-bis(2′,6′-dinitro-4′-trifluoromethylphenyl)-4,7,10-trioxa-1,13-tridecadiamine* **(12)** Into 40 ml ethanol containing 18 g (66.7 mmole) **(1)** and 7.37 g (73.0 mmole) triethylamine, 8 g (36.4 mmol) diethylene glycol bis(aminopropyl) ether was added. An exothermic reaction with formation of red colour was observed. With a magnetic stir, the reaction was proceeded at 70°C for 5.5 h. The mixture was extracted with ethyl acetate and washed with aqueous solution of NaCl. The extract was dried ($Na_2SO_4$) and evaporated to give an oil. After solving the oil with ethanol and adding a small amount of acetone, a yellow solid 22.1 g (96.4% yield) precipitated. m.p. 98–100°C. IR: 1100(s, C-F), 1280(s, C-O), 1550(s, $NO_2$), 3300(w, NH); NMR: $\delta^1H$(acetone-$d_6$): 1.60(p, 4H, C-$CH_2$-C), 2.83(m, 6H, NH and N-$CH_2$-C), 3.30(m, 12H, $OCH_2$), 8.23(s, 4H, ArH). $\delta^{19}F$(acetone-$d_6$): −15.0; MS: 689($M^+ + 1$); Anal. Calcd for $C_{24}H_{26}N_6F_6O_{11}$: C, 41.86; H, 3.78; N, 12.21; F, 16.57; Found: C, 42.22; H, 3.73; N, 12.31; F, 16.65.

*N,N′-bis(2′-amino-6′-nitro-4′-trifluoromethyl)-4,7,10-trioxa-1,13-tridecadiamine* **(13)** Into 20 ml 1,4-dioxane and 5 ml water bearing 3.44 g (5 mmole) **(12)**, 12 g ammonium sulfide (S, 8%) was added. Gradual formation of red colour was observed. The mixture was stirred at 60°C for 5 min and for 2 h at room temperature. After adding acetone and filtering sulfur powder, the evaporated oil was purified with chromatography (silica gel, acetone-petroleum ether, 1:1.5, as eluant) to produce a red solid **(13)** 2.05 g (65.3% yield). m.p. 93–94°C. IR: 1100(s, C-F), 1210(s, C-O), 1330(s, $NO_2$), 3350, 3550(m, NH, $NH_2$); NMR: $\delta^1H$(acetone-$d_6$): 1.56(p, 4H, C-$CH_2$-C), 3.10(m, 4H, $NCH_2$), 3.33(s, 6H, $OCH_2$), 4.93(b, 4H, $NH_2$), 6.00(b, 2H, NH), 6.93(s, 2H, ArH, para- to $NO_2$), 7.30(s, 2H, ArH, ortho- to $NO_2$). $\delta^{19}F$(acetone-$d_6$): −15.0; MS: 629($M^+ + 1$), 628($M^+$); Anal. Calcd for $C_{24}H_{30}N_6F_6O_7$: C, 45.86; H, 4.78; N, 13.38; F, 18.15; Found: C, 45.65; H, 4.65; N, 13.39; F, 18.22.

*1-N,N-dimethylamino-2,6-dinitro-4-benzotrifluoride* **(15)** 0.5 g (0.43 mmol) **(14)** and excess of potassium carbonate were placed in 20 ml DMF. An immediate red colour was formed. The mixture was heated to 100°C with stirring for 5.5 h. Addition of water, extraction with ethyl acetate and dryness on $Na_2SO_4$ were seccessively performed. The solution was evaporated and the residue was separated by chromatography to afford 0.3 g starting material (**14**) (60% was recovered) and 50 mg red solid (**15**) in 52% yield. m.p. 128.3–129.3°C. IR: 1100(s, C-F), 1520(s, $NO_2$), 3080(w, ArH). $\delta^1H(CCl_4)$: 2.80(6H, s, $CH_3$), 7.96(2H, s, ArH). $\delta^{19}F(CCl_4)$: −16.3; MS: 280($M^+$ + 1), 279($M^+$), 262($M^+$ + 1 − $CH_3$). Anal. Calcd for $C_9H_8N_3F_3O_4$: C, 38.71; H, 2.86; N, 15.05; F, 20.43; Found: C, 38.67; H, 2.96; N, 15.28, F, 20.31.

## ACKNOWLEDGEMENT

We thank Prof. Qing-Chuan Yang (Department of Chemistry, Beijing University) for X-ray analysis and Dr. Ze-Qi Xu for his helpful comments on the manuscript.

## REFERENCES

1. H. K. Porter, *Organic Reaction*, **20,** 455 (1973).
2. J. J. D'Amico, C. C. Tung and W. E. Dahl, *Phosphorus and Sulfur*, **7,** 143 (1979).
3. J. J. D'Amico, C. C. Tung and D. J. Dahm, *J. Org. Chem.*, **41,** 3564 (1976).
4. Chi Ching Sung, Chen Mei Jin, Wang Qi Wen and Sheng Wei, *J. Chem. Soc. Perkin Trans* **2,** to be published.
5. (a) Arthur Roe and W. F. Little, *J. Org. Chem.*, **20,** 1577 (1955). (b) R. J. Galbreath and R. K. Ingham, *J. Org. Chem.*, **23,** 1804 (1958). (c) H. L. Yale and F. Sowinski, *J. Am. Chem. Soc.*, **80,** 1651 (1958). (d) V. N. Knyazev, V. N. Drozd and V. M. Minov, *Tetrahedron Letters*, 4825 (1976).
6. (a) J. Miller, 'Aromatic Nucleophilic Substitution', Elsevier, New York, N.Y. (1968). (b) T. J. De Boer and I. P. Dirkx, 'The Chemistry of Nitro and Nitroso Groups', part 1, ed. Feuyer, H., Interscience, New York, N.Y., p 487 (1969).
7. (a) J. M. Strauss, *Chem. Rev.*, **70,** 668–691 (1970). (b) J. F. Bunnett and R. E. Zahler, *ibid*, **49** (1951). (c) F. Terrier, *ibid*, **82** (1982).
8. R. I. Cattana, J. O. Singh, J. D. Anunziata and J. J. Silber, *J. Chem. Soc. Perkin trans* **2,** 79 (1987).
9. (a) R. T. Blickenstaff and E. L. Foster, *J. Org. Chem.*, **26,** 5029 (1961). (b) K. Ueno, F. Ishikawa and T. Naito, Tetrahedron Letters, 1283 (1969). (c) C. Djerassi, N. Crossley and M. A. Kielczewski, *J. Org. Chem.*, **27,** 1112 (1962). (d) H. J. Bestman and H. Schulz, *Chem. Ber.*, **92,** 530 (1959). (e) W. Fied and P. Pfaender, *Ann.*, **64,** 111 (1961).