extracted with ether. The ethereal extract was dried, concentrated, and distilled giving 2.03 g (44.0%) of **17**: bp 205–210 °C (0.1 mm); NMR ($CDCl_3$) δ 0.23 (s, 6, $SiCH_3$), 0.39 (s, 6, $SiCH_3$), 3.39 (s, 2, NCH_2), 4.17 (s, 2, OCH_2), 6.80–7.88 (m, 14, aromatic H), and 8.07 (s, 1, CHO); ir (neat) 1675, 1720 cm^{-1} (CO).

Anal. Calcd for $C_{26}H_{31}NO_3Si_2$: C, 67.64; H, 6.77; N, 3.03. Found: C, 67.72; H, 6.49; N, 3.30.

***o*-(*N*-Methyl-*N*-dimethylphenylsilylmethylamino)benzyl Alcohol (14).** A mixture of **17** (1.17 g, 2.5 mmol) and lithium aluminum hydride (0.95 g, 25 mmol) in THF (50 ml) was heated at reflux for 3 h, and then it was hydrolyzed with 5% HCl. After the addition of ether (400 ml), the acid layer was separatd. The acid layer was made alkaline with aqueous sodium hydroxide and extracted with ether. Distillation of the extract gave 0.58 g (80.2%) of **14** which was identical with the product of lithium aluminum hydride reduction of **13**.

Acknowledgment. The authors are grateful to the Shin-Etsu Chemical Industry Co., Ltd., for a generous gift of chlorosilanes. We also wish to thank Professor Robert West, The University of Wisconsin, for helpful discussions.

Registry No.—**4g**, 60030-85-5; **4g** HCl, 60030-86-6; **7a**, 18670-77-4; **7b**, 27977-47-5; **7c**, 1833-31-4; **11**, 60030-87-7; **12**, 58617-52-0; **13**, 60030-88-8; **14**, 60030-89-9; **15**, 60030-90-2; **16**, 3342-77-6; **17**, 60030-91-3; **18a**, 43180-39-8; **18e**, 13865-52-6; **18h**, 60030-92-4; **18i**, 10316-03-7; triphenylsilyllithium, 791-30-0; methyldiphenylsilyllithium, 3839-30-3; dimethylphenylsilylmethyl chloride, 1833-51-8; chloromethylpentamethyldisilane, 5181-46-4; benzyne, 462-80-6; *o*-bromo-*N*,*N*-dimethylaniline, 698-00-0.

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Derivatives of 4-Chloro-3,5-dinitrobenzotrifluoride. 1. Synthesis of *S*,*S*'-[2,2'-Dithiobis(6-nitro-*α*,*α*,*α*-trifluoro-*p*-tolyl)] Bis(*N*,*N*-dimethylcarbamothioate) and Related Compounds[1,2]

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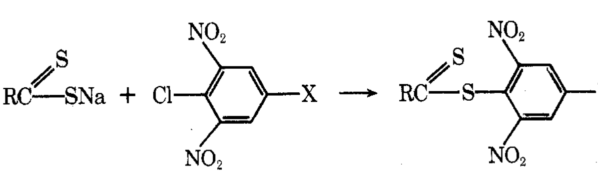
Received January 9, 1976

The reaction of sodium or triethylamine salts of disubstituted dithiocarbamic acids with 4-chloro-3,5-dinitrobenzotrifluoride afforded the unexpected novel title compounds (**4–9**). The reaction of the triethylamine salt of ethyldithiocarbamic acid with 4-chloro-3-nitrobenzotrifluoride or 4-chloro-3,5-dinitrobenzotrifluoride furnished a novel synthesis of substituted phenyl sulfides (**10–11**). Possible mechanisms and supporting NMR, ir, Raman, mass spectra, and single-crystal x-ray structure analysis for **4** are discussed.

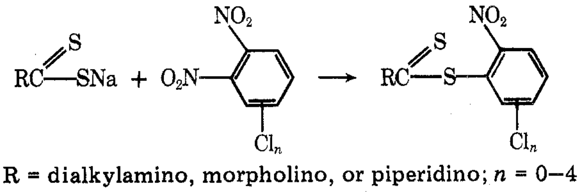
Prakasch and Mohan Lal Garg[3] reported that the reaction of activated aromatic compounds, such as 1-chloro-2,6-dinitrobenzene and 1,4-dichloro-2,6-dinitrobenzene, with sodium salts of disubstituted dithiocarbamic acids furnished the 2,6-dinitrophenyl and 4-chloro-2,6-dinitrophenyl esters of the dithiocarbamic acids, respectively.



(1)

R = morpholino or piperidino; X = H or Cl

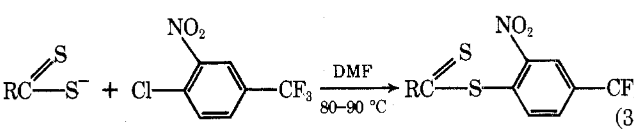
However, in more activated halogenated aromatic nitro compounds,[4] nitro groups are displaced nucleophilically and aromatic esters of dithiocarbamic acids are obtained in 72–92% yields.



(2)

R = dialkylamino, morpholino, or piperidino; *n* = 0–4

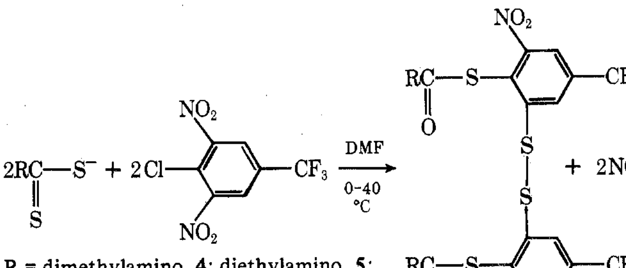
We wish to report that the reaction of sodium or triethylamine salts of disubstituted dithiocarbamic acids with 4-chloro-3-nitrobenzotrifluoride in dimethylformamide at 80–90 °C furnished the expected products (**1–3**) in 82–97% yields.



(3)

R = dimethylamino, **1**; morpholino, **2**; diethylamino, **3**

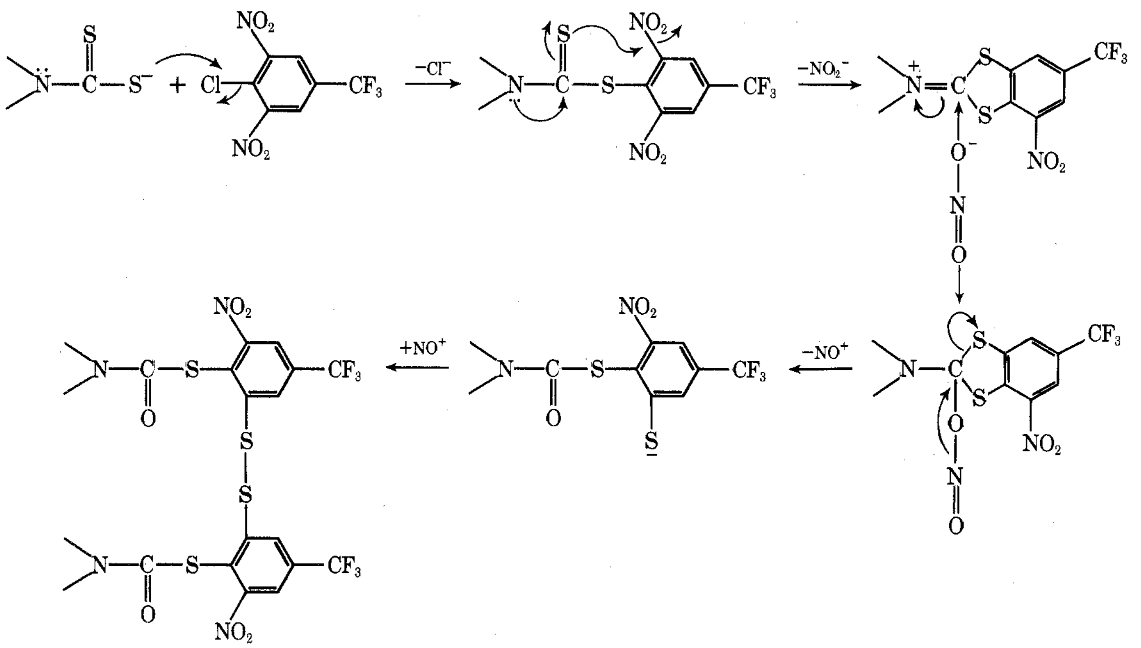
However, when 4-chloro-3-nitrobenzotrifluoride was replaced with 4-chloro-3,5-dinitrobenzotrifluoride, the expected



(4)

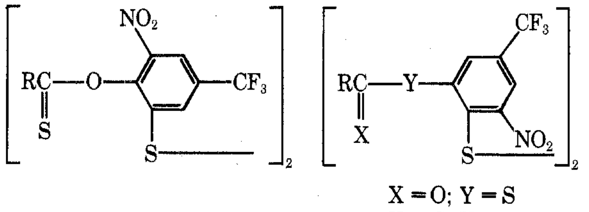
R = dimethylamino, **4**; diethylamino, **5**; pyrrolidino, **6**; piperidino, **7**; morpholino, **8**; 2,6-dimethyl morpholino, **9**

Scheme I



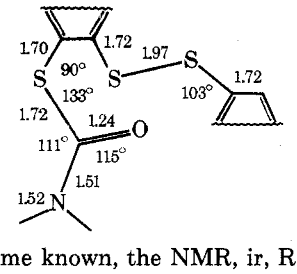
products were not obtained but instead S,S'-[2,2′-dithiobis-(6-nitro-α,α,α-trifluoro-p-tolyl)] bis(N,N-dimethylcarbamothioate) and related compounds (**4–9**) were obtained.

However, based on only elemental analysis, molecular weight, and NMR data the following three related structures had to be considered:



X = O; Y = S
X = S; Y = O

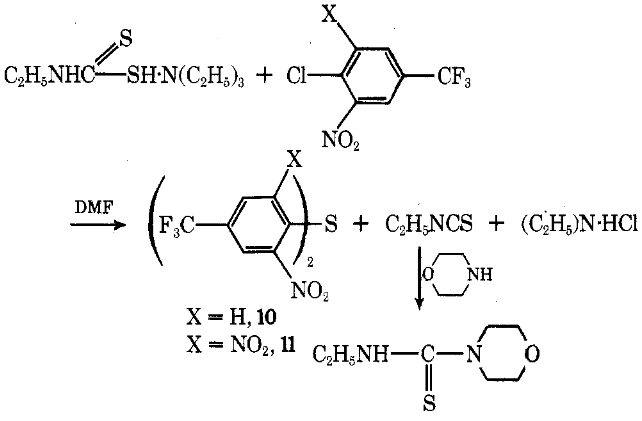
Since the NMR, ir, Raman, and mass spectral data could not completely substantiate the proposed structures **4–9**, an x-ray crystallographic study for **4** was undertaken. This study furnished conclusive and definitive proof for the proposed structures and also ruled out the above three related structures. The disulfide linkage is in the plane of both phenyl rings. The dihedral angle between the phenyl rings of the same molecule is 94°. The carbamothioate group is planar within 0.1 Å and makes a dihedral angle of 112° with the phenyl ring to which it is attached. The corresponding angle for the nitro group is 40°. The planes of the nitro and carbamothioate groups are nearly perpendicular (91°). The following drawing depicts the bond angles and distances for the dimethylcarbamothioate and disulfide groups for **4**. Once the correct



structures became known, the NMR, ir, Raman, and mass spectral data (see Table I) became more meaningful and thus provided additional support for the proposed structures. The isobutane chemical ionization mass spectrum of **4** furnished the molecular weight data in the form of $(M + 1)^+$ at m/e 651. Furthermore, the electron impact mass spectrum of **4** afforded the presence of the $(CH_3)_2N^+{=}C{=}O$ ion m/e 72 (100% – base peak) which lends support for the transformation of the >NC(=S)–S–moiety to >NC(=O)–S–. Moreover, the presence of the carbonyl (1689 cm^{-1}) and the absence of the thiocarbonyl adsorption bands in the ir spectra for **4** and **8** ruled out the presence of the >NC(=S)–O– group and thus again confirmed the conversion of the dithio to the thiolcarbamyl moiety. The presence of both the aromatic sulfide (683 cm^{-1}) and aromatic disulfide (529 cm^{-1}) adsorption bands in the Raman spectra for **4** and **8** furnished additional evidence for the proposed structures.

The proposed mechanism for this unusual reaction is depicted in Scheme I. The liberation of NO and NO_2 (formed by the oxidation of NO) gases which were collected and identified by the mass spectrometer lends support for the proposed mechanism.

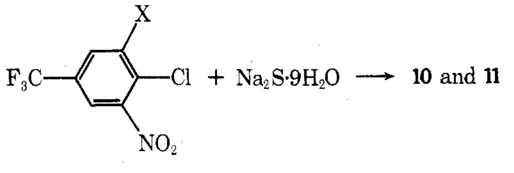
The reaction of the triethylamine salt of ethyldithiocarbamic acid with 4-chloro-3-nitrobenzotrifluoride or 4-chloro-3,5-dinitrobenzotrifluoride furnished a novel synthesis of substituted phenyl sulfides (**10, 11**).



X = H, **10**
X = NO_2, **11**

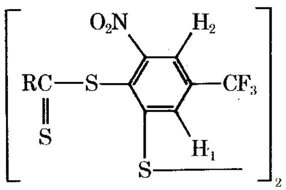
12 (5)

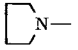
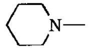
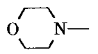
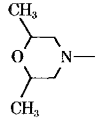
The sulfides **10** and **11** were also prepared by the following conventional method:



(6)

Table I

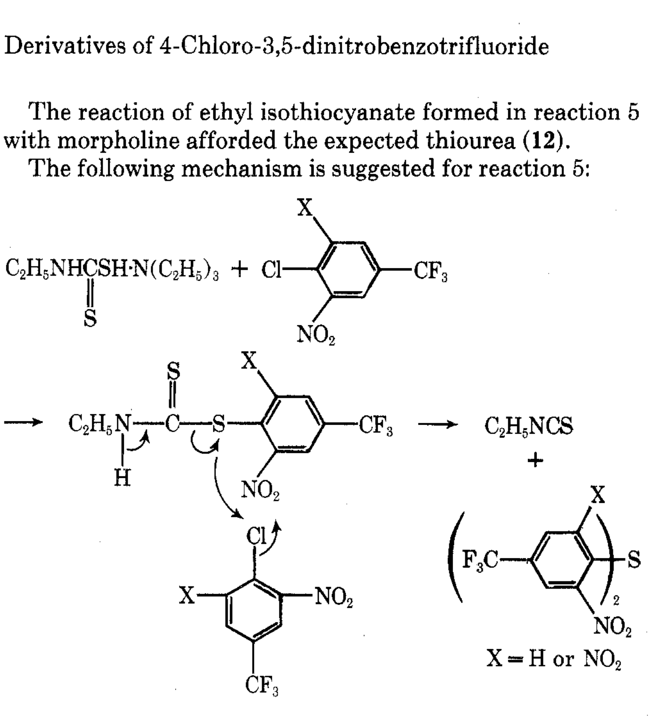


Registry no.	Compd	Method	RC(=S)–SM		Crude yield, %	Mp, °C	NMR, δ (ppm), CDCl$_3$–Me$_4$Si	Empirical formula[j]	Mol wt	
			R	M					Calcd	Found
59983-45-8	4[l]	A	$(CH_3)_2N$	Na·2H$_2$O	60	242–243[a,h,i,k]	3.1 [s, 12, $(CH_3)_2N$] 7.9 (m, 2, ArH$_1$) 8.1 (m, 2, ArH$_2$)	$C_{20}H_{16}F_6N_4O_6S_4$	650.6	650[f]
59983-46-9	5[l]	A	$(C_2H_5)_2N$	$H(C_2H_5)_3$	64	194–195[b]	1.3 (t, 12, CH_3CH_2) 3.5 (q, 8, CH_3CH_2) 7.9 (m, 2, ArH$_1$) 8.1 (m, 2, ArH$_2$)	$C_{24}H_{24}F_6N_4O_6S_4$	706.7	704[g]
		B			58					
59983-47-0	6	B		$H(C_2H_5)_3$	51	214–215[b]	2.1 (m, 8, CH_2CH_2) 3.6 (m, 8, CH_2NCH_2) 7.9 (m, 2, ArH$_1$) 8.2 (m, 2, ArH$_2$)	$C_{24}H_{20}F_6N_4O_6S_4$	702.7	700[f]
59983-48-1	7	A		$H(C_2H_5)_3$	44	186–187[c]	1.7 [br s, 12, $(CH_2)_3$] 3.6 [br s, 8, CH_2NCH_2) 7.9 (m, 2, ArH$_1$) 8.2 (m, 2, ArH$_2$)	$C_{26}H_{24}F_6N_4O_6S_4$	730.8	720[g]
59983-49-2	8[l]	A		$H(C_2H_5)_3$	96	240–241[d,h,i]	Could not obtain NMR; sample insoluble even in Me$_2$SO-d_6	$C_{24}H_{20}F_6N_4O_8S_4$		
59983-50-5	9	A		$H(C_2H_5)_3$	52	223–224[e]	1.3 (d, 12, $CH_3CHOCHCH_3$) 2.8 (br envelope, 4, $CH_3CHOCHCH_3$) 3.9 (br envelope, 8, CH_2NCH_2) 8.0 (m, 2, ArH$_1$) 8.2 (m, 2, ArH$_2$)	$C_{28}H_{28}F_6N_4O_8S_4$	790.8	780[f]

[a] Two recrystallizations from toluene. [b] Two recrystallizations from ethyl acetate. [c] Recrystallizations from 2-propanol/ethyl acetate (1:1). [d] Recrystallization from Me$_2$SO. [e] Recrystallization from acetonitrile. [f] Solvent acetone. [g] Solvent chloroform. [h] Ir (CsI): 4, 3080 and 3060 (ArC–H), 2930 (aliphatic C–H), 1689 (C=O), 1541 (NO$_2$ asym), 1368 (NO$_2$ sym), 1312 (CF$_3$ sym), 1177, 1140, and 1112 (CF$_3$ antisym), and 757, 739, and 713 cm^{-1} (CF$_3$ deformation); 8, 3060 (ArC–H), 2975, 2930, and 2860 (aliphatic CH), 1689 (C=O), 1511 (NO$_2$ asym), 1368 (NO$_2$ sym), 1312 (CF$_3$ sym), 1177, 1138, and 1112 (CF$_3$ antisym), and 755, 738, and 713 cm^{-1} (CF$_3$ deformation). [i] Raman spectra: 4, 3085 and 3057 (ArC–H), 2937 (aliphatic C–H), 1606 (ArC=C). 1364 (NO$_2$ sym), 829 (ArNO$_2$), 683 (ArCS), and 529 cm^{-1} (Ar disulfide); 8, 3054 (ArC–H), 2988, 2969, 2925, and 2858 (aliphatic CH), 1606 (ArC=C), 1361 (NO$_2$ sym), 829 (ArNO$_2$), 682 (ArCS), and 529 cm^{-1} (Ar disulfide). [j] Satisfactory analytical data (±0.4% for C, H, F, N, and S) were reported for 4–9. [k] Isobutane chemical ionization mass spectrum of 4 gave *m/e* 651 (M + 1)$^+$. [l] Electron impact mass spectra *m/e* (rel intensity): 4, 562 (0.1), 397 (0.1), 325 (0.5), 309 (4.2), 293 (0.2), 253 (0.9), 207 (0.4), 163 (0.7), 151 (0.5), 73 (3.4), 72 (100), 69 (0.9), 56 (1.7), 44 (1.7), 43 (0.7), 42 (2.3), 15 (2.2); 5, 453 (0.3), 353 (0.7), 337 (1.2), 253 (1), 207 (0.5), 163 (0.7), 151 (0.4), 101 (5.8), 100 (100), 73 (1.2), 72 (33), 69 (0.6), 42 (1.9), 29 (18); 8, 604 (0.4), 367 (0.8), 351 (7), 253 (1), 207 (0.7), 163 (0.9), 151 (0.7), 115 (5.8), 114 (100), 86 (0.8), 70 (65), 69 (1.2), 57 (1), 56 (3.6), 55 (1.5), 45 (4.8), 44 (0.7), 43 (1.2), 42 (19.5), 30 (1.4), 29 (1.6), 27 (1.3), 15 (2.1).

The reaction of ethyl isothiocyanate formed in reaction 5 with morpholine afforded the expected thiourea (**12**).

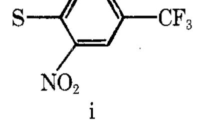
The following mechanism is suggested for reaction 5:



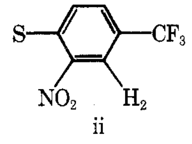
Experimental Section

NMR spectra were obtained with a Varian A-60 NMR spectrometer. The chemical shifts are reported in δ, using tetramethylsilane as reference. All melting points were taken upon a Fisher-Johns block and are uncorrected. The electron impact mass spectra of **2**, **4**, **5**, **8**, **10**, and **11** were determined with a Varian-MAT CH-7A mass spectrometer operating at an ionizing potential of 70 eV using the direct insertion probe technique with a source temperature of 250 °C. This instrument was operated in the CIMS mode to obtain the chemical ionization mass spectrum of **4**. The infrared spectra of **4** and **8** were obtained with a Beckman IR-12 spectrophotometer. The Raman spectra of **4** and **8** were obtained with a Spex Ramalog 5 system consisting of the Spex double monochromator, 1800 1/mm gratings, and photon counting detection. X ray for **4** was determined by using a Syntex $P\bar{2}_1$ and XTL using a ω scan with graphite monochromatized Mo $K\bar{\alpha}$ radiation.

2-Nitro-4-trifluoromethylphenyl Dimethyldithiocarbamate (1). To a stirred solution containing 39.2 g (0.22 mol) of sodium dimethyldithiocarbamate dihydrate in 200 ml of dimethylformamide, 45.2 g (0.2 mol) of 4-chloro-3-nitrobenzotrifluoride was added in one portion. An exothermic reaction set in causing a temperature rise from 22 to 39 °C over a 12-min period. The stirred reaction mixture was heated at 80–90 °C for 4 h and at 25–30 °C for 18 h. After cooling to 0 °C, 800 g of ice water was added and stirring continued at 0–10 °C for 30 min. The precipitate was collected by filtration, washed with water until neutral to litmus, and air dried at 25–30 °C. The crude product, mp 89–90 °C, was obtained in 97% yield. After recrystallization from 2-propanol, it melted at 105–106 °C: NMR ($CDCl_3$) δ 3.55 [s, 6, $(CH_3)_2N$], 7.85 (m, 2, fragment i), 8.25 (m, 1, fragment ii).



i



ii

Anal. Calcd for $C_{10}H_9F_3N_2O_2S_2$: C, 38.70; H, 2.92; N, 9.03; S, 20.66. Found: C, 38.86; H, 3.04; N, 9.11; S, 20.82.

2-Nitro-4-trifluoromethylphenyl Morpholinecarbodithioate (2) and 2-Nitro-4-trifluoromethylphenyl Diethyldithiocarbamate (3). To a stirred solution containing 19.2 g (0.22 mol) of morpholine or 16.2 g (0.22 mol) of diethylamine and 22.3 g (0.22 mol) of triethylamine in 200 ml of dimethylformamide, 16.7 g (0.22 mol) of carbon disulfide was added dropwise at 0–10 °C. After stirring at 25–30 °C for 2 h, 45.2 g (0.2 mol) of 4-chloro-3-nitrobenzotrifluoride was added in one portion. An exothermic reaction set in causing a temperature rise from 22 to 35 °C over a 30-min period. The stirred reaction mixture was heated at 80–90 °C for 5 h and at 25–30 °C for 18 h. After cooling to 0 °C, 800 g of ice water was added slowly over a 30-min period and stirring continued at −10 to 5 ° for 2 h. The precipitate was collected by filtration, washed with water until neutral to litmus, and air dried at 25–30 °C. **2**, mp 63–65 °C, was obtained in 82% yield. After two recrystallizations from toluene, it melted at 83–84 °C: NMR ($CDCl_3$) δ 3.8 (m, 4, $-CH_2OCH_2$), 4.2 (m, 4, $-CH_2NCH_2$), 7.83 (m, 2, fragment i), 8.25 (m, 1, fragment ii); mass spectrum *m/e* (rel intensity) 306 (20) ($M^{\cdot+} - NO_2$), 130 (35), 86 (100), 72 (13), 60 (38), 59 (14), 56 (11), 45 (14), 42 (11), 30 (12), 28 (18), and 27 (39).

Anal. Calcd for $C_{12}H_{11}F_3N_2O_3S_2$: C, 40.90; H, 3.15; F, 16.18; N, 7.95; S. 18.20. Found: C, 41.05; H, 3.15; F, 16.49; N, 7.99; S, 18.36. Mol wt calcd, 352.4; found, 354 (toluene).

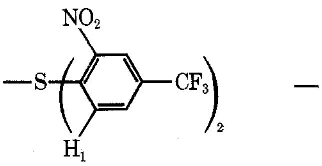
3, mp 50–55 °C, was obtained in 96% yield. After two recrystallizations from heptane it melted at 68–69 °C: NMR ($CDCl_3$) δ 1.40 (t, 6, CH_3CH_2), 3.93 (q, 4, CH_2CH_3), 7.85 (m, 2, fragment i), 8.25 (m, 1, fragment ii).

Anal. Calcd for $C_{12}H_{13}F_3N_2O_2S_2$: C, 42.60; H, 3.87; F, 16.85; N, 8.28; S, 18.95. Found: C, 42.38; H, 3.96; F, 16.57; N, 8.49; S, 18.99. Mol wt calcd, 338.4; found, 335 (benzene).

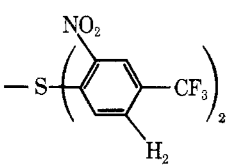
***S,S′*-[2,2′-Dithiobis(6-nitro-*α,α,α*-trifluoro-*p*-tolyl)] Bis(*N,N*-dimethylcarbamothioate) and Related Compounds. Method A (4, 5, 7, 8, and 9).** To a stirred slurry containing 0.22 mol of the sodium salt of dimethyldithiocarbamic acid and triethylamine salts of diethyl, piperidine, morpholine, or *cis,trans*-2,6-dimethylmorpholinedithiocarbamic acids[5] in 200 ml of dimethylformamide at −20 °C, 54 g (0.2 mol) of 4-chloro-3,5-dinitrobenzotrifluoride was added in small portions over a 10-min period while maintaining the temperature at −20 to −10 °C. The stirred reaction mixture was held at −10 to 0 °C for 2 h and at 25–30 °C for 24 h. During this period NO, NO_2, COS, and CS_2 were liberated. After cooling to 0 °C 600 g of ice water and 200 ml of ethyl ether were added and stirring continued at 0–10 °C for 1 h. The precipitate was collected by filtration, washed with 200 ml of ethyl ether and finally with water until the washings were neutral to litmus, and air dried at 25–30 °C.

Method B (5 and 6). To a stirred slurry containing 0.22 mol of the triethylamine salt of diethyl- or pyrrolidinedithiocarbamic acid[5] in 200 ml of dimethylformamide at room temperature, 54 g (0.2 mol) of 4-chloro-3,5-dinitrobenzotrifluoride was added in one portion. Immediately an exothermic reaction set in causing a temperature rise from 20 to 60 °C followed by the liberation of brown-yellowish colored gases. A sample of the liberated gases was collected over helium and identified as a mixture of NO, NO_2, CS_2, and COS by mass spectrometer. The reaction mixture was stirred for 24 h and the product isolated as described in method A. The data are summarized in Table I.

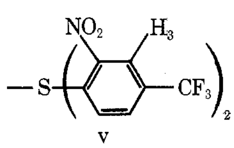
Bis(2-nitro-4-trifluoromethylphenyl) Sulfide (10). Method I. To a stirred solution containing 71.0 g (1.1 mol) of 70% ethylamine and 111.4 g (1.1 mol) of triethylamine in 200 ml of dimethylformamide, 83.4 g (1.1 mol) of carbon disulfide was added dropwise at 0–10 °C. After stirring at 25–30 °C for 1 h, 225.6 g (1.0 mol) of 4-chloro-3-nitrobenzotrifluoride was added in one portion. An exothermic reaction set in causing a temperature rise from 24 to 59 °C over a 10-min period. The reaction mixture was stirred at 25–30 °C for 1 day. After the addition of 1700 ml of water and 700 ml of ethyl ether stirring was continued for 30 min. The solid was collected by filtration, washed with water until the washings were neutral to litmus, and air dried at 25–30 °C. The crude product (**10**), mp 131–133 °C, was obtained in 77% yield. After two recrystallizations from heptane–ethyl acetate (3:1) **10** melted at 146–147 °C: NMR (Me_2SO-d_6) δ 7.70 (d, 2, fragment iii), 8.00 (d, 2, fragment iv), 8.65 (s, 2, fragment v); mass spectrum *m/e* (rel intensity) 412 (74.2) ($M^{\cdot+}$), 393 (48), 322 (53), 318 (84), 302 (57), 166 (45), 160 (62), 146 (44), 126 (54), and 30 (100).



iii



iv



v

Anal. Calcd for $C_{14}H_6F_6N_2O_4S$: C, 40.79; H, 1.47; F, 27.65; N, 6,79; S, 7.78. Found: C, 40.80; H, 1.45; F, 27.66; N. 6.68; S, 7.54.

The separated ether layer from the filtrate was washed with water until the washings were neutral to litmus and dried over sodium sulfate. The ether was removed in vacuo at a maximum temperature of 30 °C at 40 mm. The residue was filtered to remove a small amount of impurities and distilled in vacuo. Ethyl isothiocyanate, bp 59–60

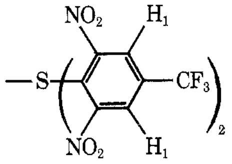
°C (60 mm), n^{25}D 1.5105, was obtained in 68% yield: NMR ($CDCl_3$) δ 1.40 (t, 3, $-CH_3$), 3.65 (q, 2, $-CH_2$).

Anal. Calcd for C_3H_5NS: C, 41.35; H, 5.78; N, 16.07. Found: C, 41.24; H, 5.82; N, 16.15.

Method II. Conventional. 10 was prepared as described by Roe and co-workers.[6] A mixture melting point with the product obtained by method I was not depressed and the NMR spectra of the two were identical.

Anal. Calcd for $C_{14}H_6F_6N_2O_4S$: C, 40.79; H, 1.47; F, 27.65; N, 6.79; S, 7.78. Found: C, 40.74; H, 1.36; F, 27.44; N, 6.80; S, 7.95.

Bis(2,6-dinitro-4-trifluoromethylphenyl) Sulfide (11). Method I. To a stirred solution containing 12.9 g (0.2 mol) of 70% ethylamine and 22.3 g (0.22 mol) of triethylamine in 250 ml of tetrahydrofuran, 15.2 g (0.2 mol) of carbon disulfide was added dropwise at 0–10 °C. After stirring at 25–30 °C for 1 h, the reaction mixture was cooled to −20 °C. A solution containing 54 g (0.2 mol) of 4-chloro-3,5-dinitrobenzotrifluoride in 200 ml of tetrahydrofuran was added dropwise at −20 to 0 °C in 30 min. The reaction mixture was stirred at 25–30 °C for 1 day. After the addition of 1 l. of water and 400 ml of heptane, the reaction mixture was stirred at 25–30 °C for 30 min. The solid was collected by filtration, washed successively with water until neutral to litmus and with 200 ml of heptane, and air dried at 50 °C. The crude product (**11**), mp 186–188 °C, was obtained in 48% yield. After recrystallization from isopropyl alcohol–ethyl acetate (5:1) **11** melted at 203–204 °C: NMR (Me_2SO-d_6) δ 8.85 (s, 4, fragment vi); mass spectrum *m/e* (rel intensity) 502 (6.1) ($M\cdot^+$), 483 (6.7), 362 (11.0), 316 (6.6), 175 (7.6), 173 (9.7), 163 (10.1), 145 (7.6), 143 (36), 119 (6.9), 107 (7.6), 69 (15), and 30 (100).



vi

Anal. Calcd for $C_{14}H_4F_6N_4O_8S$: C, 33.48; H, 0.80; F, 22.70; N, 11.15; S, 6.38. Found: C, 33.61; H, 0.79; F, 22.92; N, 11.22; S, 6.40.

Method II. Conventional. To a stirred mixture containing 26.5 g (0.11 mol) of sodium sulfide monohydrate and 150 ml of dimethylformamide at −20 °C, 54 g (0.2 mol) of 4-chloro-3,5-dinitrobenzotrifluoride was added in one portion. External cooling was removed and the reaction mixture was stirred at 25–30 °C for 4 days. After the addition of 800 ml of water, stirring was continued at 10–20 °C for 2 h. The solid was collected by filtration, washed with water until neutral to litmus, and air dried at 25–30 °C. Crude **11**, mp 187–189 °C, was obtained in 84% yield. After recrystallization from heptane–ethyl acetate (2:1), **11** melted at 203–204 °C. A mixture melting point with product obtained from method I was not depressed and the NMR spectra of the two were identical.

Anal. Calcd for $C_{14}H_4F_6N_4O_8S$: C, 33.48; H, 0.80; F, 22.70; N, 11.15; S, 6.38. Found: C, 33.44; H, 0.78; F, 22.97; N, 11.03; S, 6.10.

***N*-Ethyl-4-morpholinothiocarboxamide (12).** To 8.7 g (0.1 mol) of ethyl isothiocyanate (derived from method I) in 30 ml of heptane, 8.7 g (0.1 mol) of morpholine was added in one portion. An exothermic reaction set in causing a temperature rise from 22 to 60 °C. The stirred reaction mixture was heated at reflux for 5 h. After cooling to 25 °C, the solid was collected by filtration and air dried at 25–30 °C. Crude **12**, mp 60–61 °C, was obtained in 98% yield. After recrystallization from heptane–ethyl acetate (2.5:1), **12** melted at 61–62 °C: NMR ($CDCl_3$) δ 1.25 (t, 3, CH_3), 3.82 (q and s, 10, CH_2 + morpholino), 5.90 (br s, 1, NH). A mixture melting point with an authentic sample was not depressed and the NMR spectra of the two were identical.

Anal. Calcd for $C_7H_{14}N_2OS$: C, 48.28; H, 8.10; N, 16.08; S, 18.40. Found: C, 48.14; H, 8.13; N, 16.00; S, 18.33.

X-Ray Crystallography for 4.[7] Crystal Data (from Single-Crystal X-Ray Diffractometry). Radiation: Mo $K\bar{\alpha}$ (graphite monochromatized, parallel mode), $\lambda = 0.71069$ Å; unit cell (monoclinic), $a = 5.265$ (4) Å, $b = 11.505$ (8) Å, $c = 22.32$ (4) Å, $\alpha = 91.4$ (1)°, $z = 2$, $V = 1337$ Å^3; space group $P211$ (a unique); $d_x = 1.62$ g cm^{-3}; $d_m = 1.61$ g cm^{-3} (by flotation); absorption coefficient 4.3 cm^{-1} (not applied).

Intensity Data. Intensity measurements for 1057 reflections were made using a variable rate ω scan holding the detector arm fixed during data collection. Space group equivalences were averaged and reflections for which $I < 3\sigma(I)$ were discarded, leaving 494 reflections on which to base a structure determination and refinement.

Structure Determination. Structure solution was by direct methods via MULTAN.[8] Five E maps were calculated before the phase set was tried which revealed 32 atom positions. A difference Fourier showed six additional positions, leaving only two fluorines not located. When attempts to refine the positional parameters by full matrix least squares failed, inspection of the deduced positions showed approximate centrosymmetry[9] of the structure. This relationship was used to calculate the remaining atom positions. The positional parameters were refined by Fourier techniques and the thermal parameters by block diagonal least squares. Final agreement was to a conventional $R = 0.13$. Each of the two molecules in the unit cell has one of its halves related to the other by a twofold axis. In addition, the two symmetry independent molecular halves are approximately related by a center of symmetry at $(x, y, z) = (3/8, 1/4, 1/4)$. The space group symmetry is thus approximately $P2/n11$, although $0kl$ reflections were observed for which $k + l = 2n + 1$.

Acknowledgment. The assistance of R. W. Fuhrhop and F. L. May is kindly appreciated.

Registry No.—**1**, 59983-51-6; **2**, 59991-82-1; **3**, 59983-52-7; **10**, 365-55-9; **11**, 59983-53-8; **12**, 59983-54-9; sodium dimethyldithiocarbamate, 128-04-1; 4-chloro-3-nitrobenzotrifluoride, 121-17-5; morpholine, 110-91-8; diethylamine, 109-89-7; diethyldithiocarbamic acid Et_3N, 2391-78-8; piperidinedithiocarbamic acid Et_3N, 59983-55-0; morpholinedithiocarbamic acid Et_3N, 23336-68-7; *cis*-2,6-dimethylmorpholinedithiocarbamic acid Et_3N, 59983-57-2; 4-chloro-3,5-dinitrobenzotrifluoride, 393-75-9; pyrrolidinedithiocarbamic acid Et_3N, 59983-58-3; ethyl isothiocyanate, 542-85-8; carbon disulfide, 75-15-0; sodium sulfide, 1313-82-2; *trans*-2,6-dimethylmorpholinedithiocarbamic acid Et_3N, 59983-60-7.

Supplementary Material Available. An atomic coordinate table (1 page). Ordering information is given on any current masthead page.

References and Notes

(1) Presented at First Chemical Congress of the North American Continent, Mexico City, Mexico, Dec 1975.

(2) Presented at VIIth International Symposium on Organic Sulfur Chemistry, Hamburg, Germany, July 13, 1976.

(3) S. Prakasch and De Mohan Lal Garg, *J. Indian Chem. Soc.*, **42,** 412 (1965); D. Mohan Lal Gag, *ibid.*, **42,** 415 (1965); *Chem. Abstr.*, **63,** 11562 (1965).

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(5) E. Morita and J. J. D'Amico, *Rubber Chem. Technol.*, **44,** 881 (1971).

(6) A. Roe et al., *J. Org. Chem.*, **21,** 28 (1956).

(7) Observed and calculated structure factors are available from Dr. D. J. Dahm.

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