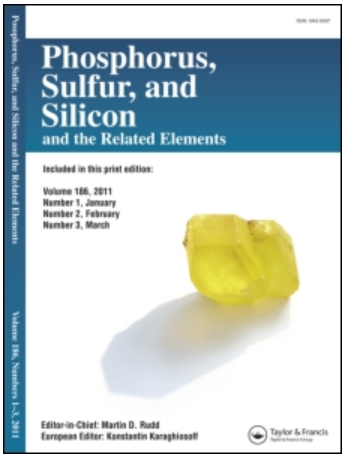

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DERIVATIVES OF 4-CHLORO-3,5-DINITROBENZO-TRIFLUORIDE. IV. SYNTHESIS OF BIS [6-(ETHYLTHIO)-5-NITRO-α,α,α-TRIFLUORO-*m*-TOLYL] DISULFIDE (1) AND ETHYL 2,6-DINITRO-α,α,α-TRIFLUORO-*p*-TOLYL SULFIDE (2)

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DERIVATIVES OF 4-CHLORO-3,5-DINITROBENZOTRIFLUORIDE. IV. SYNTHESIS OF BIS [6-(ETHYLTHIO)-5-NITRO-α,α,α-TRIFLUORO-*m*-TOLYL] DISULFIDE (1) AND ETHYL 2,6-DINITRO-α,α,α-TRIFLUORO-*p*-TOLYL SULFIDE (2)

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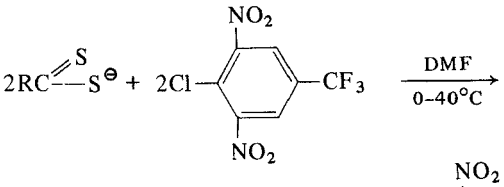
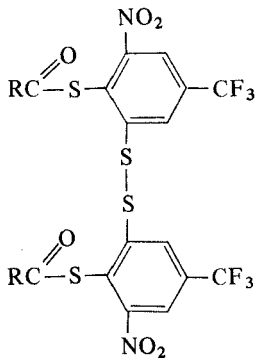
The reaction of potassium ethyl dithiocarbonate with 4-chloro-3,5-dinitrobenzotrifluoride in dimethylformamide at 25-30°C afforded the titled disulfide (1) and sulfide (2). Possible mechanism and supporting NMR, ir, Raman and mass spectral data are discussed. The assigned structure for 1 was verified by X-ray crystal structure analysis.

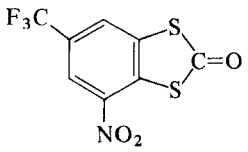
In the first communication of this series[1] we reported that the reaction of sodium or triethylamine salts of disubstituted dithiocarbamic acids with 4-chloro-3,5-dinitrobenzotrifluoride afforded the products illustrated below.



R = dimethylamino, diethylamino, pyrrolidino, piperidino, morpholino.



In a particular example (R = dimethylamino), K. Rasheed and J. D. Warkentin[2] repeated our work and reported the isolation of two products, the above disulfide [R = $-N(CH_3)_2$] and 4-nitro-6-trifluoromethyl-1,3-benzodithiol-2-one

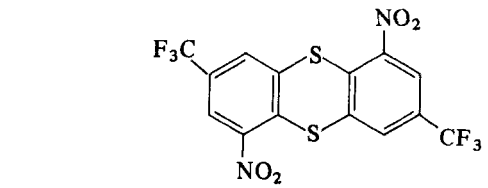


We failed to isolate the latter compound because we extracted and washed our crude product with ethyl ether, and thereby inadvertently discarded the ether soluble 1,3-benzodithiol-2-one.

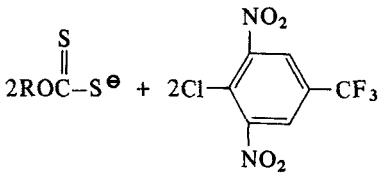
In a recent communication[3] we reported that the reaction of potassium ethyl or isopropyl dithiocarbonate with 4-chloro-3,5-dinitrobenzotrifluoride in DMF at 80-90°C afforded 1,6-dinitro-3,8-bis(trifluoromethyl)-thianthrene. However, when this reaction was repeated using only potassium ethyl dithiocarbonate and the above halogen compound in DMF at 25-30°C, two unexpected products 1 and 2 were obtained in 36 and 23% yields, respectively.

However, based on only elemental analysis, molecular weight and NMR data, the following alternative structure A had to be considered for 1.

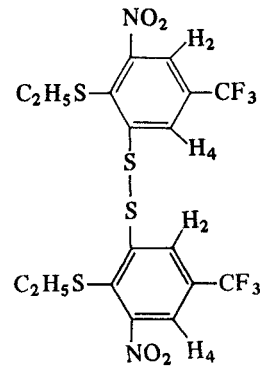
Since the NMR, ir, Raman and mass spectral data could not completely substantiate the proposed structure 1, an X-ray crystallographic study for 1 was undertaken. As noted in Figure 1, this study furnished conclusive and definitive proof for the proposed structure 1 and thus ruled out structure A. The disulfide linkage is very nearly in the plane of both phenyl rings (maximum deviation–0.1 Å). The angle formed by the two phenyl rings is about 98°. The planes of the nitro groups are rotated by 58° out of the planes of their respective rings. Once the correct structure 1 became known, the NMR, ir, Raman and mass spectral data (see experimental section) became more meaningful and thus provided additional support for the proposed structure 1. The electron impact mass spectrum of 1 furnished the molecular weight data in the form of M^+ at m/e 564. The presence of



R = $-C_2H_5$ and $-CH(CH_3)_2$ ↑ DMF 80–90°C 28 hr

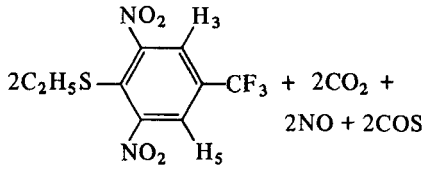


R = $-C_2H_5$ only ↓ DMF 25–30°C 13 days



1

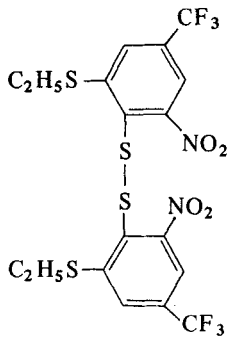
+



2

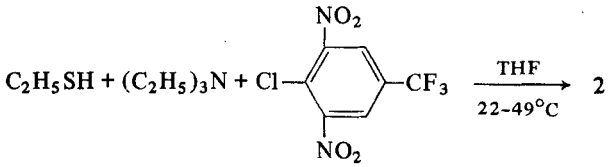
both the ethyl sulfide (636 cm^{-1}) and aromatic disulfide (504 cm^{-1}) adsorption bands in the Raman spectra for **1** furnished additional evidence for the proposed structure **1**.

The possible mass spectral fragmentation route for **1** is shown in Scheme 1.



Structure A

Proof of structure for **2** was established by the following conventional reaction:



The proposed mechanism for this unusual reaction is depicted in Scheme 2. The liberation of CO_2, COS, NO and NO_2 (formed by the oxidation of NO) gases, which were collected and identified by mass spectrometry, lends support for the proposed mechanism.

EXPERIMENTAL

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 **1** was 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. The infrared spectra of **1** was obtained with a Beckman IR-12 spectrophotometer. The Raman spectra of **1** was obtained with a Spex Ramalog 5 system consisting of the Spex double monochromator, 1800 1/mm gratings, and photon counting detection. X-ray for **1** was determined by using a Syntex $P2_1$ and XTL using a ω scan with graphite monochromatized Mo $K\bar{\alpha}$ radiation.

Bis[6-(ethylthio)-5-nitro-α,α,α-trifluoro-m-tolyl] Disulfide (1) and ethyl 2,6-dinitro-α,α,α-trifluoro-p-tolyl sulfide (2)
To a stirred solution containing 129.7 g (0.66 mol) of potassium ethyl dithiocarbonate dihydrate in 500 ml of dimethylformamide at −20°C, 162 g (0.60 mol) of 4-chloro-3,5-dinitrobenzotrifluoride was added in small portions over a 10-min period while maintaining the temperature below 10°C. The reaction mixture was stirred at 25–30°C for 13 days. During this period, NO, NO_2, COS, and CO_2 were liberated. A sample of these gases was collected over helium and identified by mass spectrometry. After cooling to 5°C, 650 ml of ethyl

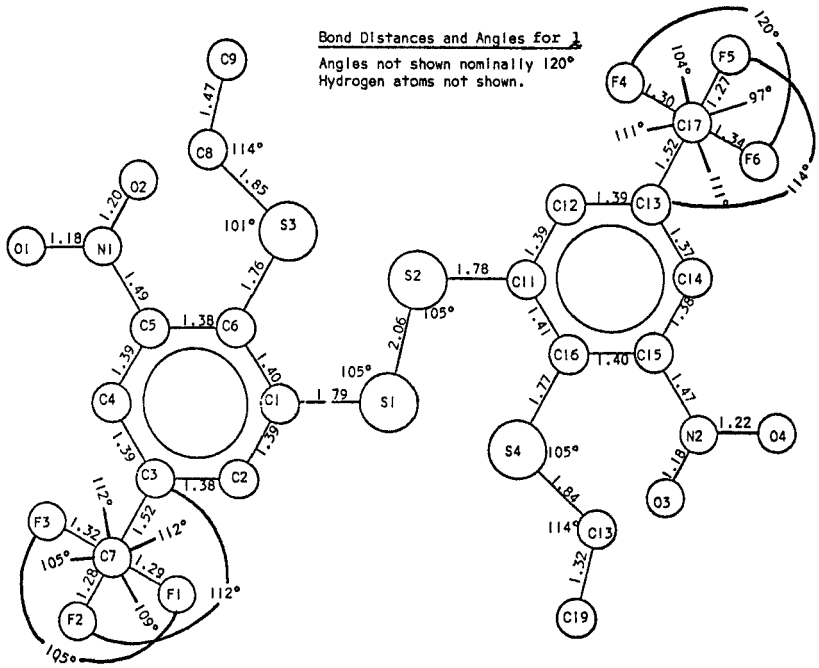


FIGURE 1 Bond Distances and Angles for **1**. Angles not shown nominally 120°. Hydrogen atoms not shown.

ether and 2000 g of ice water were added and stirring continued at 25–30°C for 2 hr. The precipitate was collected by filtration, washed with 250 ml of ethyl ether and finally with water until the washings were neutral to litmus and air-dried at 50°C. The crude product (**1**), mp 178–180°C, was obtained in 36% yield. After recrystallization from ethyl acetate **1** melted at 188–189°C: NMR ($CDCl_3$, sat. soln.) δ 1.36 (t, 6, SCH_2CH_3); 3.10 (q, 4, SCH_2); 7.74 (m, 2, H_2); 7.93 (m, 2, H_4); mass spectrum m/e (rel intensity), 564 (17.4), 284 (9.7), 283 (13.3), 282 (100), 254 (43.1), 207 (9.0), 190 (13.7), 178 (4.7), 163 (8.5), and 29 (33.9). Ir(CsI): 3080 (ArC–H), 2980, 2940, and 2880 (aliphatic CH), 1607 (ArC=C), 1541 (NO_2 asym.), 1453 (CH_3 deform.), 1440 and 1420 (CH_2 deform.), 1368 (NO_2 sym.), 1312 (CF_3 sym.), 1178, 1145 and 1112 (CF_3 antisym.) and 753, 739 and 712 cm^{-1} (CF_3 deform.). Raman spectra: 1603 (ArC=C), 1362 (NO_2 sym.), 827 (Ar–NO_2), 636 (C_2H_5S–C), and 504 cm^{-1} (Ar disulfide).

Anal. Calcd for $C_8H_{14}F_6N_2OS$: C, 38.29; H, 2.50; F, 20.19; N, 4.96; S, 22.72; mol. wt. 564.6. Found: C, 38.37; H, 2.49; F, 20.10; N, 4.93; S, 22.79; mol. wt. 570 ($CHCl_3$).

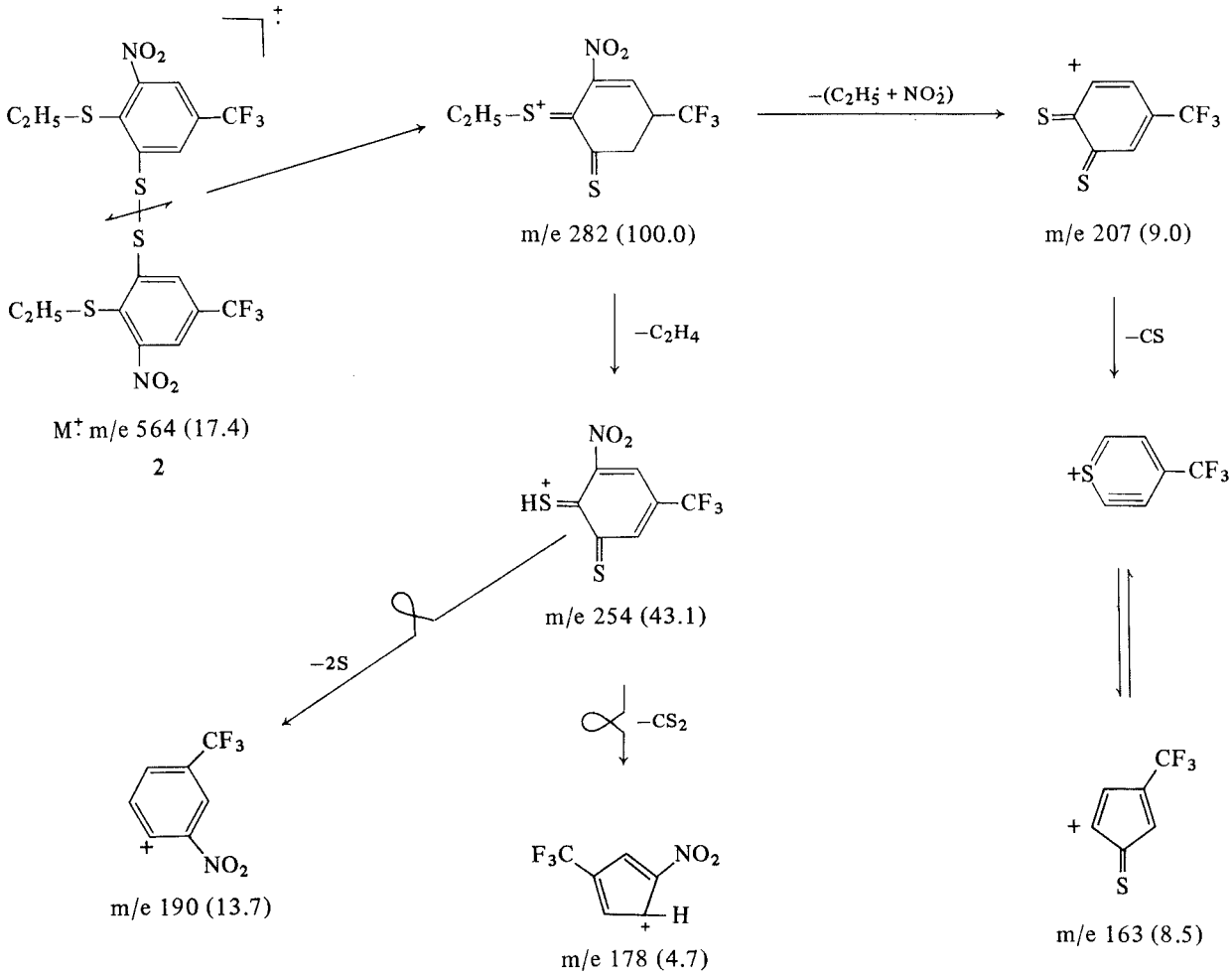
The ethyl ether of the filtrate was removed *in vacuo*. The filtrate was extracted with four 450 ml portions of chloroform. The combined chloroform extracts were washed with water until neutral to litmus, dried over sodium sulfate and the chloroform removed *in vacuo* on a rotary evaporator at a maximum temperature of 70°C at 1–2 mm. The residue (78 g) was slurried with 300 ml of chloroform and filtered to remove 2 g of impurities. The filtrate was diluted with chloroform to a volume of 400 ml. One-fourth (100 ml) of this solution was slurried with 75 g of silica gel and the solvent removed *in vacuo* at maximum temperature of 90°C at 1–2 mm. This mixture was added to a column containing 525 g of silica gel in 60/40 mixture of cyclohexane/chloroform. Elution with 60/40 mixture of cyclohexane/chloroform gave 10 g (23%) of **2**, mp 84–86°C. After recrystallization from heptane, **2** melted at 91–92°C. NMR ($CDCl_3$) δ 1.2 (t, 3, SCH_2CH_3); 2.90 (q, 2, SCH_2); 8.00 (s, 2, H_3 and H_5).

Anal. Calcd for $C_9H_7F_3N_2O_4S$: C, 36.49; H, 2.38; F, 19.24; N, 9.46; S, 10.82. Found: C, 36.64; H, 2.21; F, 19.21; N, 9.29; S, 11.06.

2 *(conventional method)* To a stirred solution containing 6.2 g (0.1 mol) of ethyl mercaptan, 10.3 g (0.1 mol) of triethylamine and 100 ml of tetrahydrofuran, 27 g (0.1 mol) of 4-chloro-3,5-dinitrobenzotrifluoride was added in one portion. An exothermic reaction set in causing a temperature rise from 22 to 49°C. The reaction mixture was stirred at 25–30°C for 1 day. After the addition of 800 g of ice water stirring was continued at 0–10°C 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 (**2**), mp 89–90°C, was obtained in 95% yield. After recrystallization from heptane **2** melted at 91–92°C. A mixture melting point with the product obtained from the former method was not depressed and the NMR spectra of the two were identical.

Anal. Calcd for $C_9H_7F_3N_2O_4S$: C, 36.49; H, 2.38; N, 9.46; S, 10.82. Found: C, 36.50; H, 2.42; N, 9.49; S, 10.88.

X-ray Crystallography for **1**.[4] Crystal Data. From single crystal diffractometry (MoKα, λ = 0.71069 Å): a = 18.62(1), b = 9.88(1), c = 12.58(2), β = 103.43(9), V = 2250 $Å^3$; D_m = 1.656 $g\text{-}cm^{-3}$, D_x = 1.666 $g\text{-}cm^{-3}$; z = 4; space group: $P2_1/n$.



Scheme 1

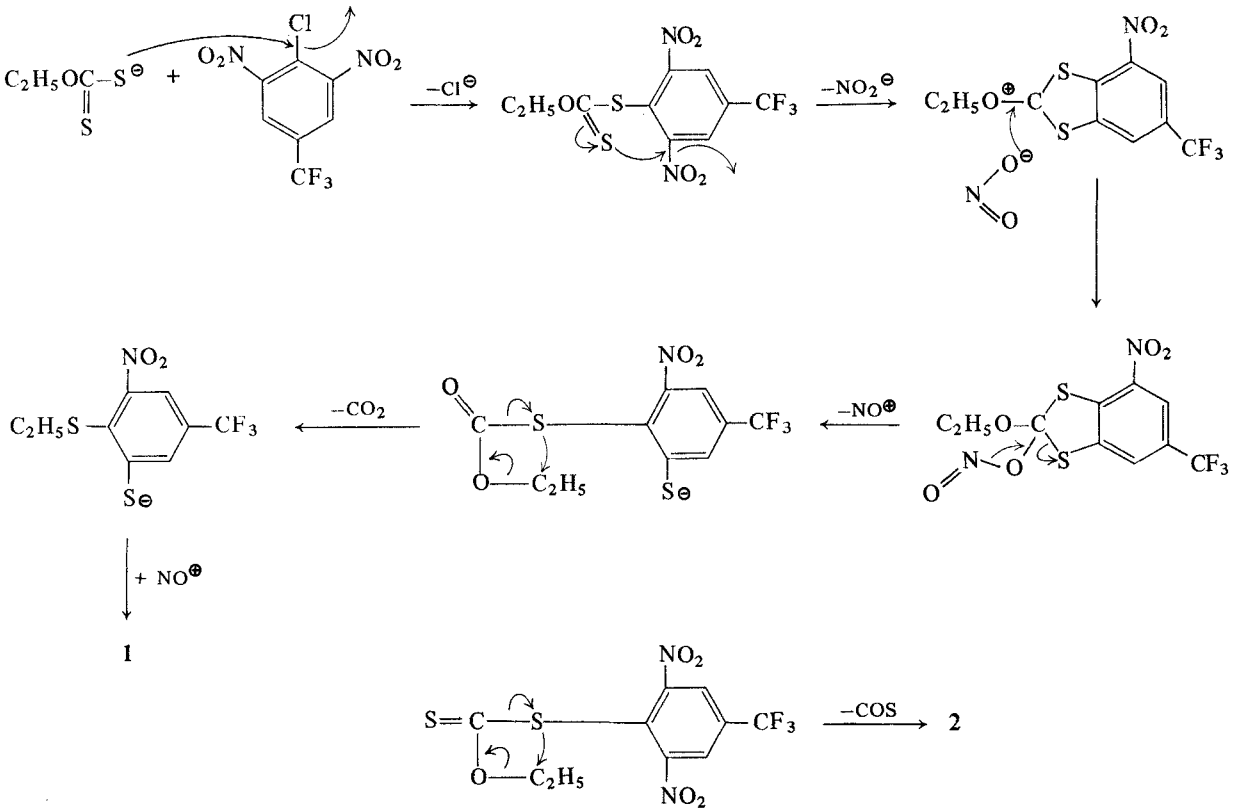
Data Collection. Instrument: Syntex $P2_1$. Crystal size: 0.45x 0.08 x 2.33 mm; absorption coefficient: 5.0 cm^{-1} (not applied) Intensity data were collected using a variable rate ω-scan with the detector arm fixed. Measurements for 6810 reflections gave data for 4714 reflections greater than 1.96σ (I) and 3622 greater than 4σ (I).

Structure Determination Syntex XTL. Using the phase set with the highest figure of merit generated by MULTAN,[5] 26 of the 34 non-hydrogen atom positions were located on an E-map. A Fourier synthesis revealed the remaining 8 atoms. Full matrix least squares refinement gave R = 0.211 with all atoms isotropic for F(OBS) > 1.96σ and R = 0.101 with all atoms anisotropic for F(OBS) > 4.0σ. A difference Fourier revealed several peaks in the vicinity of C18 and C19, an indication of disorder. Large anisotropic β's for C18 and C19 tend to substantiate this. There appeared to be considerable rotation of the trifluoromethyl groups, also indicated by high anisotropic β's. A disordered model, allowing the occupancy factors of the atoms around the ethyl group to vary, refined to a conventional R = 0.092 but gave occupancy factors greater than reasonable.

Our purpose was to determine the molecular configuration, and having accomplished this, no effort to further refine the structure was made. The 3061 largest reflections, enough to over determine an anisotropic refinement by a factor of 10, were used for the final refinement.

ACKNOWLEDGMENT

The assistance of R. W. Fuhrhop and F. L. May is kindly appreciated. We are also indebted to Dr. Peter Beak, of the University of Illinois, for helpful suggestions concerning our proposed mechanism.



Scheme 2

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4. Final parameters and a list of observed and calculated structure factors are available from Dr. D. J. Dahm.
5. G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.* **A27**, 368 (1971).