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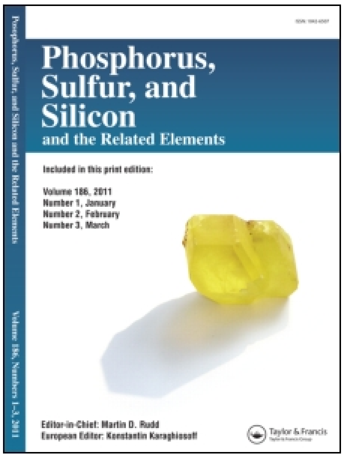

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SYNTHESIS OF 2-(2,6-DINITRO-a,a,a-TRIFLUORO-p-TOLYLIMINO)-3-(2,6-DINITRO-a,a-a-TRIFLUORO-p-TOLYL)BENZOTHIAZOLINE (1) AND 2-(METHYLIMINO)-3-(2,6-DINITRO-a,a,a-TRIFLUORO-p-TOLYL)BENZOTHIAZOLINE (2)

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SYNTHESIS OF 2-(2,6-DINITRO-α,α,α-TRIFLUORO-*p*-TOLYLIMINO)-3-(2,6-DINITRO-α,α-α-TRIFLUORO-*p*-TOLYL)BENZOTHIAZOLINE (1) AND 2-(METHYLIMINO)-3-(2,6-DINITRO-α,α,α-TRIFLUORO-*p*-TOLYL)BENZOTHIAZOLINE (2)

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The reaction of 2-amino or 2-methylaminobenzothiazole with 4-chloro-3,5-dinitrobenzotrifluoride in dimethylformamide afforded the titled benzothiazolines (1) and (2), respectively. Possible mechanism and supporting nmr, ir and mass spectral data are discussed.

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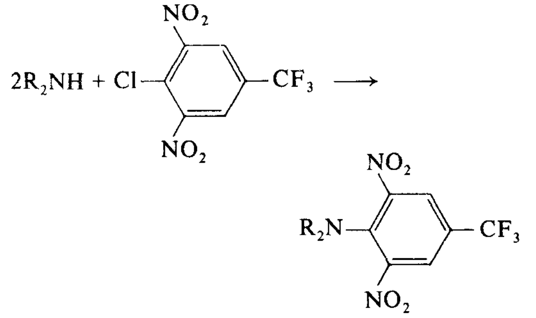
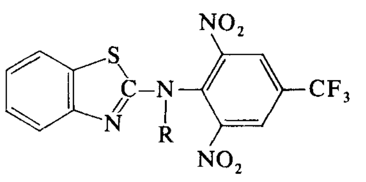
Q. F. Soper[1] reported that the reaction of 4-chloro-3,5-dinitrobenzotrifluoride with dialkylamines furnished the *N,N*-dialkyl 4-trifluoromethyl 2,6-dinitroanilines.



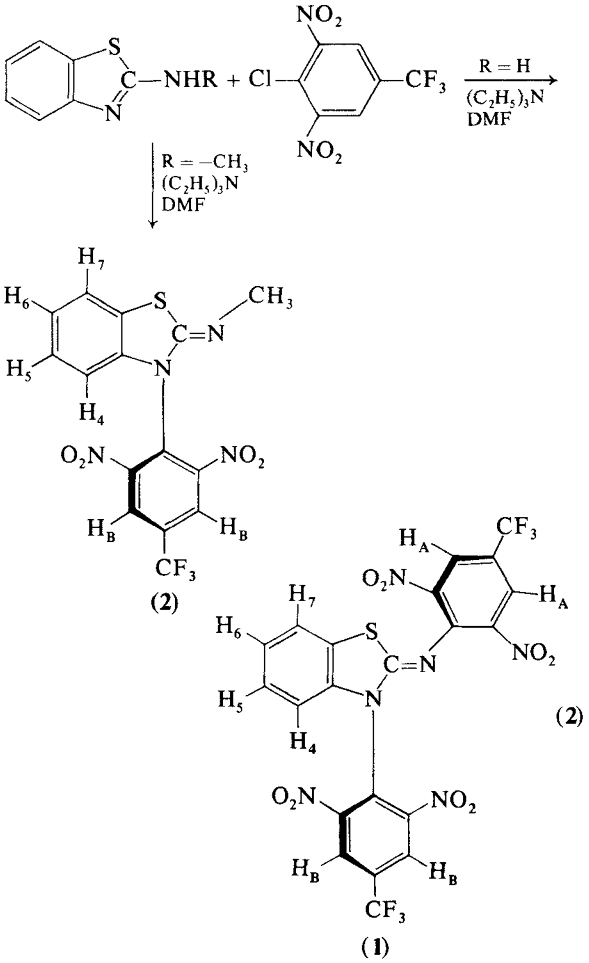
(1)

It was anticipated that replacing the dialkylamines in the above reaction with 2-amino or 2-methylaminobenzothiazole would have afforded the following analogous products:

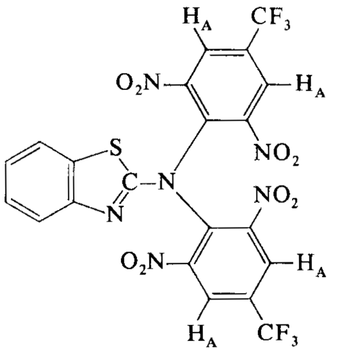


R = H and $-CH_3$

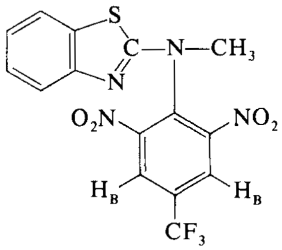
However, this was not realized for the reaction of 2-amino or methylaminobenzothiazole with the above halogen compound in DMF containing triethylamine at 80–90°C furnished the titled benzothiazolines (1) and (2) in 31 and 67% yields, respectively.



However, based on elemental analysis and molecular weight data the following alternate structures A and B had to be considered for (**1**) and (**2**), respectively.

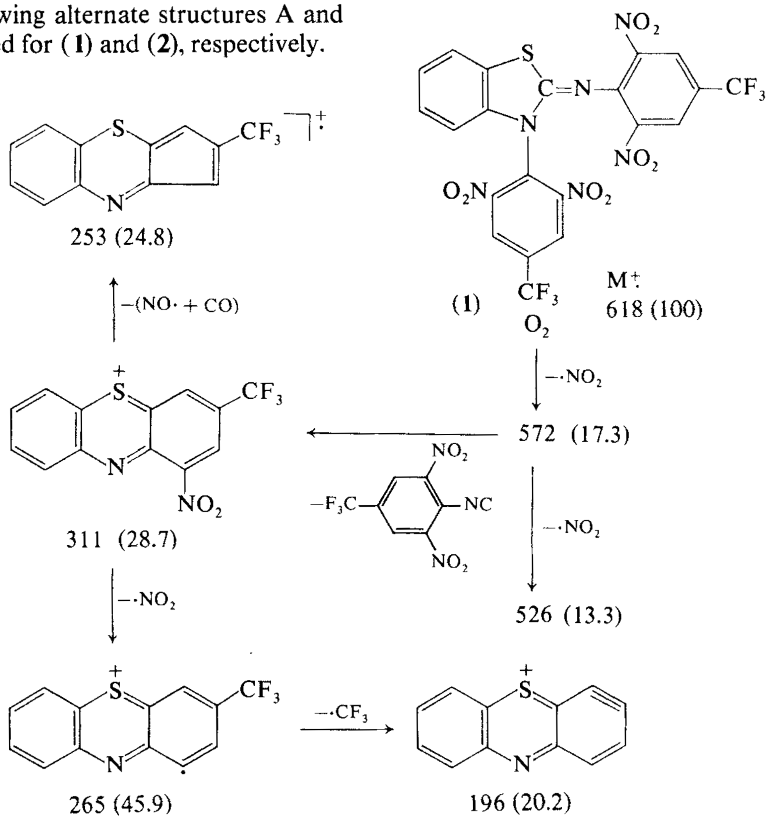


Structure A



Structure B

The nmr (^{1}H and ^{19}F), ir, and mass spectral data (see experimental section) confirmed the assigned structure (**1**) and thus ruled out structure A. If rotation in structure A was restricted, which is actually the case because of the presence of the bulky nitro groups in the 2 and 6 position, one would obtain an AB spectrum for the H$_A$ protons (i.e. four peaks) and not two singlets (δ = 8.50 and 8.95) which were actually observed., Moreover, the ^{19}F nmr further confirmed structure (**1**), since two singlets of equal intensity appeared at 110.5 and 111.2 ppm downfield from C_6D_6 which is in the expected region for C_6H_5—CF_3 group. The electron impact mass spectrum of (**1**) furnished the molecular weight data in the form of M‡ at *m/e* 618. Moreover, the spectral data (nmr-^{1}H and ^{19}F, ir, and mass spectrum) confirmed structure (**2**). The ^{19}F chemical shift at 102.4 ppm furnished additional proof for assigned structure (**2**). The ^{19}F chemical shift difference between (**2**) (102.4 ppm) and (**1**) (110.5 and 111.2 ppm) is probably due to additional deshielding effects of the aromatic rings in (**1**). The electron impact mass spectrum of (**2**) furnished the molecular ion 398.



SCHEME 1

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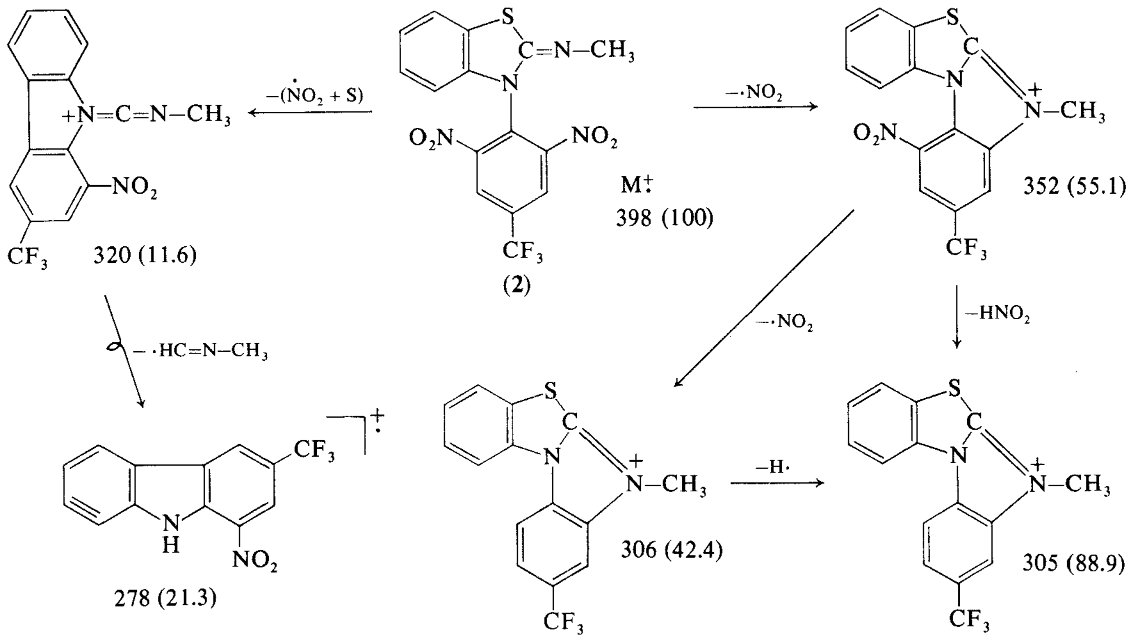
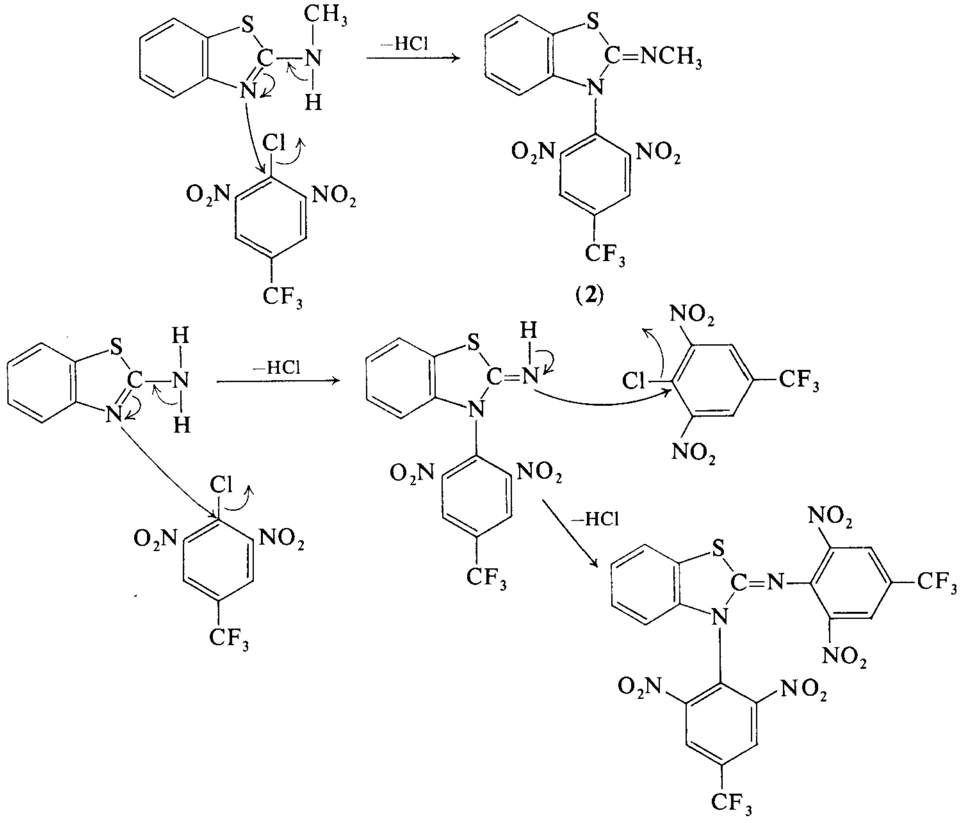


SCHEME 2



SCHEME 3 (1)

The reaction of 2-amio and 2-methylamino benzothiazole with one or two less active halogen compounds, such as methyl or benzyl and *p*-nitrophenyl halides is in progress.

Interpretation of mass fragmentation patterns for (**1**) and (**2**) are depicted in Schemes 1 and 2, respectively. The proposed mechanism for reaction (**2**) is depicted in Scheme 3.

EXPERIMENTAL

Proton nmr spectra were obtained with a Varian T-60 nmr spectrometer. The chemical shifts are reported in δ, using tetramethylsilane as reference. ^{19}F nmr spectra were obtained with a Varian A 56/60 spectrometer operated at 56.4 MHz. The chemical shifts are reported in ppm, using $CFCl_3$ as reference. All melting points were taken upon a Fisher-Johns block and are uncorrected. The electron impact mass spectra of (**1**) and (**2**) 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. The infrared spectra of (**1**) and (**2**) were obtained with a Beckman IR-12 spectrometer.

2-(Methylamino)benzothiazole (intermediate). To a stirring charge containing 770 g (10.0 mol) of 40% methylamine, 205 g (1.2 mol) of 2-chlorobenzothiazole was added in one portion. An exothermic reaction set in causing a temperature rise from 28°C to 60°C over a 1 h period. The reaction mixture was stirred at 25–30°C for 1 day. After the addition of 700 ml of water, the solid was collected by filtration, washed with water until neutral to litmus, and air-dried at 25–30°C. The product, mp 142–143°C, was obtained in 95% yield. After recrystallization from isopropyl alcohol, the melting point remained unchanged: nmr ($Me_2SO{-}d_6$) δ2.80 (d, 3, $-NHCH_3$), 6.7–7.7 (m, 4, 4ArH), 7.9 (br q, 1, $-NH$).

Anal. Calcd for $C_6H_8N_2S$: N, 17.06; S, 19.53. Found: N, 16.95; S, 19.37.

2-(2,6-Dinitro-α,α,α,-trifluoro-p-tolylimino)-3-(2,6-dinitro-α,α,α-trifluoro-p-tolyl)benzothiazoline (**1**). To a stirred solution containing 30 g (0.2 mol) of 2-aminobenzothiazole[2] and 22.3 g (0.22 mol) of triethylamine in 200 ml of dimethylformamide, 54 g (0.2 mol) of 4-chloro-3,5-dinitrobenzotrifluoride was added in one portion. The stirred reaction mixture was heated at 80–90°C for 2 h and then at 25–30°C for 18 h. After cooling to 5°C, 800 g of ice water and 300 ml of ethyl ether were added and stirring continued at 25–30°C for 2 h. The solid was collected by filtration, washed with 400 ml of ethyl ether and finally with water until the washings were neutral to litmus and air-dried at 25–30°C. The crude product (**1**), mp 301–302°C, was obtained in 31% yield. After recrystallization from isopropyl alcohol and ethyl acetate (1 : 1) (**1**) melted at 303–304°C. ^1H nmr ($Me_2SO{-}d_6$) δ6.75–7.38 (m, 3, H_5, H_6, H_7), 7.45–7.80 (m, 1, H_4), 8.50 (s, 2, H_A), 8.95 (s, 2, H_B); ^{19}F nmr (MeC = O) two singlets of equal intensity at 110.5 and 111.2 ppm downfield from C_6D_6, in expected region for $C_6H_5{-}CF_3$ group; mass spectrum *m/e* (rel intensity), 618 (100), 572 (17.3), 526 (13.3), 311 (28.7), 265 (45.9), 253 (24.8), 196 (20.2), 96 (26.6), 44 (17.4) and 30 (62.3). Ir (CsI): 3080 (ArC–H), 1650 and 1622 (C=N), 1596 (C=C), 1557 (NO_2 asym), 1475 (Ar ring mode), 1350 (NO_2 sym), 1320 and 1310 (CF_3 sym), 1180 and 1145 (CF_3 asym), 910 (CH wag, on 1,2,3,5-tetrasubt. C_6H_6), 750 (CH wag on 1,2-disubst. C_6H_6) and 723 cm^{-1} (CF deform).

Anal. Calcd for $C_{21}H_8F_6N_6O_8S$: C, 40.79; H, 1.30; F, 18.43; N, 13.59; S, 5.19. Found: C, 40.66; H, 1.58; F, 18.26; N, 13.32; S, 5.05.

2-(Methylimino)-3-(2,6-dinitro-α,α,α-trifluoro-p-tolyl)benzothiazoline (**2**). To a stirred solution containing 32.9 g (0.2 mol) of 2-(methylamino)benzothiazole and 22.3 g (0.22 mol) of triethylamine in 200 ml of dimethylformamide, 54 g (0.2 mol) of 4-chloro-3,5-dinitrobenzotrifluoride was added in one portion. The stirred reaction mixture was heated at 80–90°C for 24 h. After cooling to 25°C, 800 g of ice water, 400 ml of petroleum and 300 ml of heptane were added and stirring continued at 25–30°C for 3 h. The solid was collected by filtration, washed with water until neutral to litmus, then finally with 300 ml of heptane and air-dried at 25–30°C. The crude product (**2**), mp 120–125°C, was obtained in 67% yield. After recrystallization from isopropyl alcohol (**2**) melted at 153–154°C. ^1H nmr ($Me_2SO{-}d_6$) δ3.32 (s, 3, $= NCH_3$), 6.75–7.45 (m, 3, H_5, H_6, H_7), 7.45–7.95 (m, 1, H_4), 8.78 (s, 2, H_B); ^{19}F nmr (Me_2 C=O) one singlet at 102.4 ppm downfield from C_6D_6; mass spectrum *m/e* (rel intensity), 398 (100), 352 (55.1), 306 (42.4), 305 (88.9), 292 (18.1), 278 (21.3), 135 (14.5), 109 (31.4), 108 (27.9) and 69 (19.7). Ir (CsI): 3080 (ArC–H), 2880 ($N{-}CH_3{-}CH$), 1632 (C=N), 1595 (C=C), 1550 and 1525 (NO_2 sym), 1435 (Ar ring mode), 1415 ($CH_3{-}N$ methyl CH deform), 1355 (NO_2 asym), 1312 (CF_3 sym), 1177, 1146 and 1118 (CF_3 asym) and 715 cm^{-1} (CF deform).

Anal. Calcd for $C_{15}H_9F_3N_4O_4S$: C, 45.23; H, 2.28; F, 14.31; N, 14.07; S, 8.05. Found: 45.27; H, 2.25; F, 14.09; N, 14.11; S, 8.00.

ACKNOWLEDGMENT

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REFERENCES AND NOTES

1. Quentin F. Soper, U.S. Patent 3,257,190 dated June 21, 1966.
2. Purchased from Aldrich Chemical Company, Inc.

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