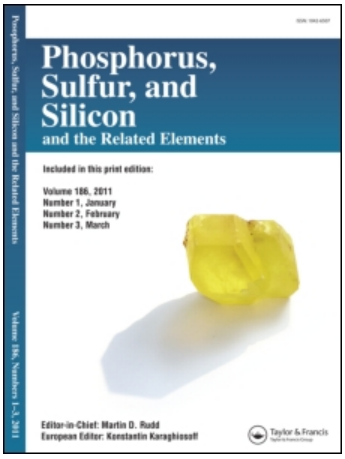

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SYNTHESIS AND SPECTRAL STUDIES OF SOME ARYL SULFIDES AND SULFONES

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The reaction of 2-chloro-1,3,5-trinitrobenzene (picryl chloride) and an equivalent amount of arylthiolate (R = H, CH_3, OCH_3, Br, Cl, NO_2) gave 2-arylthio-1,3,5-trinitrobenzenes (**1–6**). It is found that the chemical shifts of H-4,6 gave good linear relationship with Hammett σ constants indicating that the inductive effect of the substituents of the arylthio moieties is transmitted to the picryl ring through the sulfur atom. Meanwhile the reaction of picryl chloride with two fold arylthiolate gave 1,2-*bis* arylthio-3,5-dinitrobenzenes (**9–13**) except with 4-nitrobenzenethiolate. The ^{1}H NMR spectra of *bis* arylthio compounds indicate that these sulfides exist in a skew conformation. The oxidation of *bis* arylthio compounds with $KMnO_4$ gave the corresponding 1,2-*bis*-arylsulfonyl-3,5-dinitrobenzenes (**15–19**). Fragmentation processes using tandem mass spectrometry (MS/MS) in relation to structure and substituent are discussed.

Keywords: Arylthiotrinitrobenzene; *bis* arylthiodinitrobenzene; *bis*-arylsulfonyl dinitrobenzene, ^{1}H NMR

INTRODUCTION

Arylthiolate anions were known to effect halogen displacement in reactions with benzyl halide derivatives[1–10], activated and unactivated halobenzenes[11–12]. It was also reported that the nucleofugicity of an activated nitro group was unexpectedly high when the nucleophile was benzenethiolate anion[12]. In connection to our work on the reactivity of halogeno nitrobenzene with sodium arylthiolates[11], we here report a simple high yield synthesis of aromatic thioethers

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which can be effected in a one-pot treatment of 2-chloro-1,3,5-trinitrobenzene (Picryl Chloride: PC) with sodium arylthiolates. As part of this work, fragmentation patterns of the products are investigated.

RESULTS AND DISCUSSION

The reaction of PC and arylthiols using 1 : 1 molar ratio in presence of catalytic amount of sodium metal in ethanol at room temperature gave 2-(4-substituted phenylthio)-1,3,5-trinitrobenzenes **(1–6)** as indicated from elemental analyses (Exp. Part) and ^{1}H NMR, Table I.

^{1}H NMR spectra of compounds **(1–6)** indicate the presence of two types of signals corresponding to methyl, methoxy and to aromatic protons which have various appearances according to the aromatic substitution pattern, Table I.

1-6

1, R = H; 2, R = CH_3 ; 3, R = OCH_3
4, R = Br; 5, R = Cl; 6, R = NO_2

In general, the aromatic protons of the arylthio ring appear as two doublets except in case of compound **(1)** (R = H). H-4 and H-6 in the nitro ring appear as highly deshielded singlet because of their location between two nitro groups.

TABLE I ^{1}H NMR Data of 2-Arylthio-1,3,5-trinitrobenzenes **(1–6)** and PC

Cpd.	*R*	δ *ppm (DMSO-d_6)*		
		H-4,6(s)	H-2′,6′(d)	H-3′,5′(d)
1	H	8.76	7.17 (m,H-4′)	
2[a]	CH_3	8.75	7.25	7.15
3[b]	OCH_3	8.74	7.18	6.73
4	Br	8.78	7.19	7.48
5	Cl	8.78	7.27	7.34
6	NO_2	8.83	8.07	7.53
PC		8.57		

[a] CH_3 protons appear at δ 2.37 (s) ppm;
[b] OCH_3 protons appear at δ 3.73 (s) ppm.

These protons are found to be more deshielded compared to the same protons in PC because the arylthio group has electron withdrawing effect more than the chlorine atom[13].

The chemical shift of H-4 and H-6 protons are slightly different depending on the R-substituent, Table I. A plot of the chemical shift of H-4,6 of sulfides (**1–6**) against Hammett σ constants gave a linear relationship, Figure 1, indicating that the R-substituents have a regular discipline on the chemical shift of these protons. It is likely that the inductive effects of the R-substituents are being transmitted to the picryl ring through the sulfur atom, or that their presence sufficiently alters the π-could density on the picryl ring so as to affect the observed shift of H-4,6 protons. Applying the dual substituent pramater correlation (DSP) reveal diminution in transmission of resonance effect to the picryl ring atom[14].

The effect of R-substituent of the compounds under investigation is different when compared to 2,4-dinitrophenyl sulfides, which exist in a skew conformation where the *ortho* hydrogen of the nitro ring was shielded by the ring current of the neighbouring thioaryl ring[11]. Consequently, the different behavior effect of R-substituent in our compounds may be due to the diminution of resonance

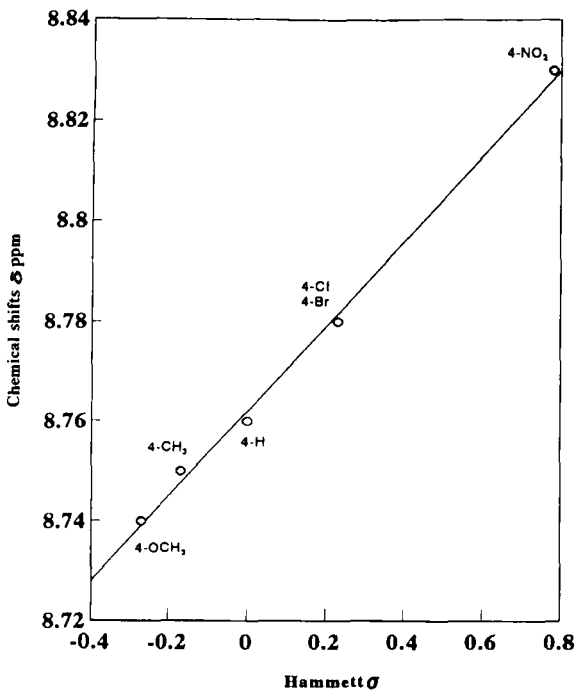
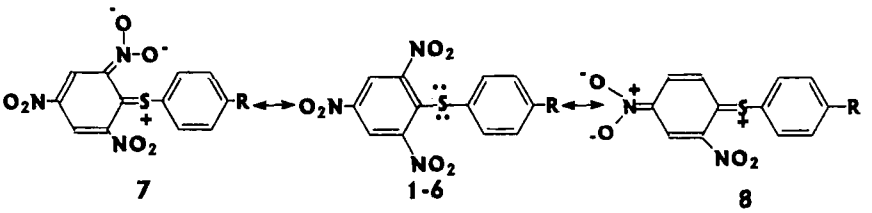


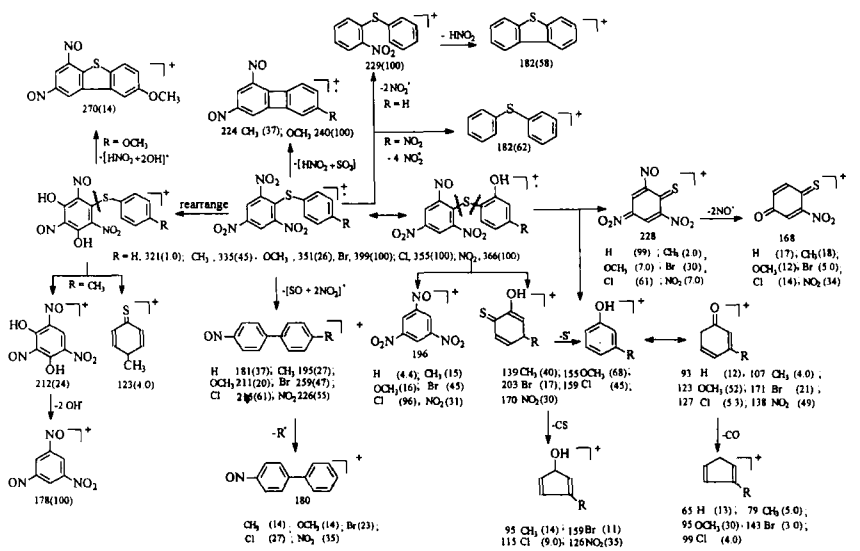
FIGURE 1 Plot of the chemical shifts of H-4,6 in (1–6) against Hammett σ constants.

between R-substituent and sulfur atom. Otherwise, a strong resonance between sulfur atom and nitro groups of picryl ring occurs giving resonating structures (**7** and **8**) which permit a feasible inductive effect of R-substituent on H-4 and H-6[14].



The work described here sought to detect and locate a general pattern for the dissociation of 2-arylthio-1,3,5-trinitrobenzenes (**1–6**), 1,2-bis-arylthio-2,5-dinitrobenzenes and (**9–13**) and 1,2-bis-arylsulfonyl-3,5-dinitrobenzenes (**15–19**).

The resulting fragmentation pathways of compounds (**1–6**) are shown in Scheme **1**. All six compounds except **1** are characterised by a strong molecular ion (base peak) in their spectra. The rearranged parent ion[15–19] undergoes **C–S** scission giving a nitroso dinitrophenylthio ion at m/z 228 and a 3-substituted phenol. This latter ion is also envisaged to arise from the degradation of 4-substituted-2-hydroxyphenylthio ion which is a product of a different **C-S** bond cleavage of the rearranged molecular ion together with the nitroso dinitro-



SCHEME 1

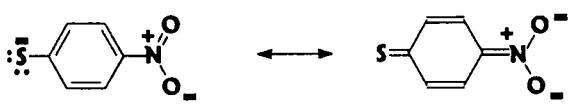
phenyl ion at m/z 196. Elimination of two NO$^{\cdot}$ from the nitroso dinitrophenylthio ion is typical to all six compounds and leads to a 2-nitro-4-thiophenoxy ion at m/z 168. While no further fragmentation is observed for the nitrosodinitorphenyl ion at m/z 196, the 4-substituted-2-hydroxphenylthio ions experience concerted expulsion of S$^{\cdot}$, CS and CO to produce three daughter ions namely 3-substituted phenol, 3-substituted hydroxypenta-dienyl and 3-substituted pentadiene ions.

Without exception, all sulfides exhibited loss of [SO + $2NO_2$]$^{\cdot}$ leading to a 4-nitroso-4′-substituted biphenyl ion. Further loss of the R-substituent gives a 4-nitrosobiphenyl ion. This fragmentation pattern has not been reported before and might prove a useful diagonestic tool for the screening of polynitroaromatic sulfides.

Complementary substituted dinitrosobiphenylene ions at m/z 224 (R = CH_3) and 240 (R = OCH_3, base peak) resulting from the loss of [HNO_2 + SO_2] are also observed, due to the dissociation of the molecular ions of compounds **2** and **3**. These compounds display also upon rearrangement either loss of [HNO_2 + 2 OH]$^{\cdot}$ leading to a methoxydinitrosothiocarbazole ion at m/z 270, or experience a different C-S bond cleavage to produce a tolylthio ion (m/z 123) and a penta substituted phenyl ion at, m/z 212. Further ejection of two OH$^{\cdot}$ from the later ion gives rise to a dinitrosonitrophenyl ion[20] at m/z 178 (R = CH_3, base peak).

Two expected diphenylsulfide ions at m/z 182, (**6**, R = NO_2) and a nitrodiphenylsulfide ion at m/z 229 (R = H, base peak), are also observed following the loss of 4 $NO_2^{\cdot}$, and 2 $NO_2^{\cdot}$ respectively. Further degradation of the latter ion produces a thiocarbazole ion at m/z 182.

The reaction of PC with two fold arylthiolate ion under the previous conditions afforded in few minutes a yellow precipitate. Elemental analyses, ^{1}H NMR and mass spectra indicate the presence of two arylthio groups and the formation of *bis* arylthiodinitrobenzenes (**9–13**) except in the case of 4-nitrobenzenethiolate. The nitro group displacement was attributed to the other nitro groups[21]. While the failure of 4-nitrobenzene thiolate to form *bis* arylthio compound is due the decreasing of its nucleophilicity by dispersing the negative charge on the sulfur atom *via* resonance structure (**14**).



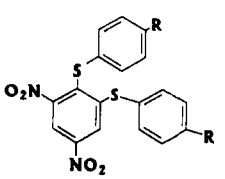
14

Two possible products are yielded from the reaction of PC with two fold of arylthiolate ions: the first is obtained from the displacement of the chlorine atom affording compounds (**1–6**) which react further with another arylthiolate ion to

replace the *ortho* nitro group with respect to the arylthio group first introduced giving 1,2-*bis*-arylthio-3,5-dinitrobenzenes. The second probable product is 2,5-*bis*-arylthio-1,3-dinitrobenzenes which came from arylthiolation-dechlorination and arylthiolation-denitration at 2 and 5 positions, respectively.

^{1}H NMR spectra of the *bis* arylthio compounds **(9–13)** show that the aromatic protons have various appearances, Table II. Protons 2′,2″,3′,3″,5′ and 5″ of the two arylthio moieties, in general, appear as doublets corresponding to superposition of signals. The data show a doublet at δ 7.60–7.67 (1H, J = 2Hz, due to meta splitting pattern) indicating that this proton resonates relatively up field than the protons of compounds **(1–6)**, picryl chloride and those reported for the proton located between two nitro groups[11,22,23]. On the other hand, the doublet at δ 8.10–8.23 (1H, J = 2Hz) resonates at the same field of the proton located between two nitro groups[11,22,23]. 4′ and 4″-Methyl and methoxy substituents reveal two sets of signals suggesting the presence of two unequivalent conformational arylthio moieties. The methyl and methoxy groups that resonate at low field can be assigned to those attached to the arylthio group adjacent to the nitro group at position 3.

Accordingly, the structure of *bis* arylthio compounds **(9–13)** agrees with the previous ^{1}H NMR data as 1,2-bis-arylthio-3,5-dinitrobenzene and not as 2,5-bis arylthio-1,3-dinitrobenzene.



9-13

9, R = H; 10, R = CH_3 ; 11, R = OCH_3; 12, R = Br; 13, R = Cl

TABLE II ^{1}H NMR data of 1,2-bis-arylthio-2,5-dinitrobenzenes (9–13)

Cpd	*R*	*δ ppm (DMSO-d_6)*					
		H-4[a] (d)	H-6[b] (d)	H-2′,6′ (d)	H-2″,6″ (d)	H-3′,5′ (d)	H-3″,5″ (d)
9	H	8.18	7.65		7.52–7.30		
10	CH_3[c]	8.15	7.63	7.38	7.31	7.24	7.12
11	OCH_3[d]	8.10	7.60	7.15	6.73	6.85	6.52
12	Br	8.21	7.62	7.66	7.61	7.43	7.43
13	Cl	8.23	7.67	7.50	7.42	7.30	7.24

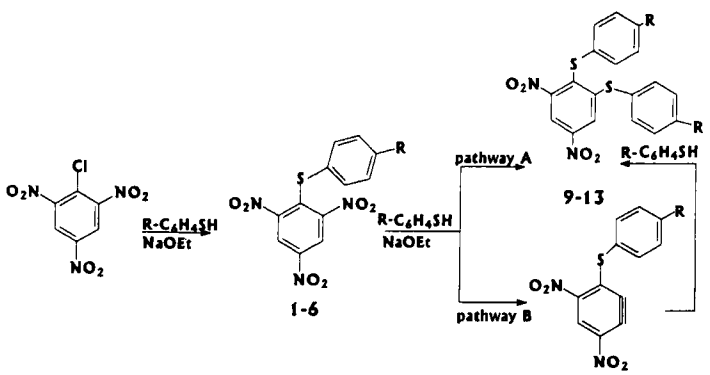
[a] $J_{4,6}$ = 2Hz
[b] $J_{6,4}$ = 2Hz
[c] methyl protons appear at δ 2.39 (s) and 2.37 (s) ppm;
[d] methoxy protons appear at δ 3.79 (s) and 3.71 (s) ppm.

The replacement of nitro group by the second arylthiolate ion to give 1,2-*bis*-arylthio-3,5-dinitrobenzene **(9–13)** is consistent with that reported earlier where the displaced nitro group was *ortho* (position 2) to methylthio function and *meta* (position 3) to an electronegative substituent[21]. The effect seen with meta electronegative functions might involve stabilization of the transition state through *sigma*-bond interaction or perhaps influence the reduction potential of the nitro group, thus eliminating the alternative possibility[21].

Ionic mechanism is suggested in order to account for the previous reaction, Scheme **2**. A normal nucleophilic substitution of the chlorine atom gives compounds **(1–6)**, which followed by normal substitution of the nitro group at position 1 (or 3), leading directly to the product **(9–13)**, pathway A. Arylthiolate (NaOEt) promoted elimination for compounds **(1–6)** yield arylthio-5,6-dehydro-2,4-dinitrobenzyne intermediate. This undergoes a regiospecific addition of arylthiol to give compounds **(9–13)**, path B. The differentiation between the two mechanisms is in progress.

The ^{1}H NMR spectra of the novel *bis* arylthio compounds **(9–13)** showed that H-6 resonated at somewhat higher field and splitted to a doublet compared to the same proton in compounds **(1–6)** and PC. The rational of this observation is given by considering the role of an additional group instead of a nitro one. The comparatively higher shielding of H-6 is presumably due to the molecule assuming skew conformation where this hydrogen lies below the adjacent arylthio ring at C-1 and experiences its diamagnetic shielding[22].

Table II reveals that the shielded H-6 vary according to the 4′-substituents attached to the arylthio group. This observation confirms the fact that the two aromatic rings come so close that the ring current of the ring bearing 4′-substituent shields H-6 of the picryl ring giving an additional evidence to the presence of disulfides **(9–13)** in the skew conformation[24,25].

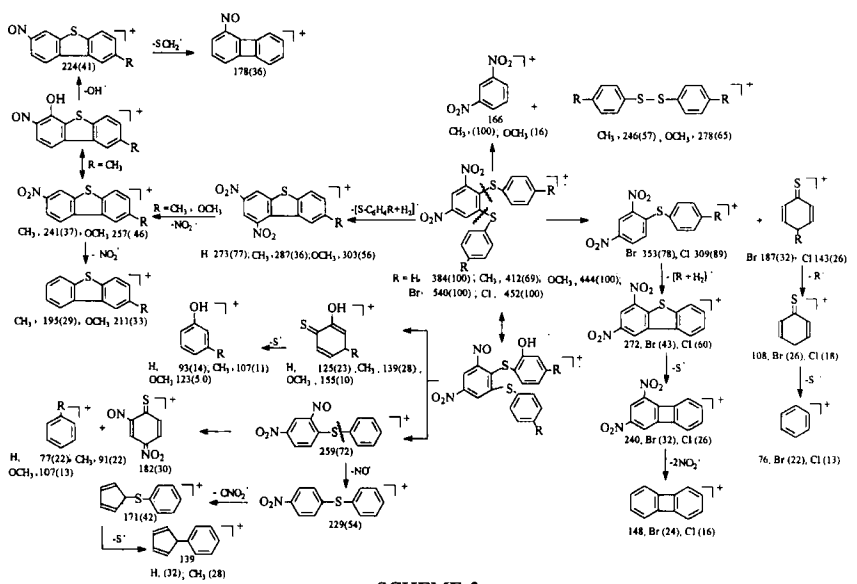


SCHEME 2

The mass spectra of the disulfides (**9–13**) demonstrate highly abundant molecular ion, and contains three major fragmentation pathways, Scheme 3. The first decomposition route comprises formation of a substituted dinitrothiocarbazole ion (**9**, R = H; **10**, R = CH_3; **11**, R = OCH_3) following the loss of a 4-substituted phenylthio radical and a molecule of a hydrogen. Successive elimination of 2 $NO_2^{\cdot}$ produces a substituted thiocarbazole ion (**10** and **11**). The substituted nitrothiocarbazole (**10**, R = CH_3) also exhibits rearrangement and degradation giving rise to a nitrosobiphenylene ion at m/z 178 following the loss of $OH^{\cdot}$ and$SCH_2^{\cdot}$, respectively. Two disulfides ions at m/z 246 and 278, next to a dinitrophenyl ion at m/z 166 (base peak, **10**, R = CH_3) are also observed through the splitting of the parent ions **10** and **11**.

The nitrosonitrodiphenylsulfide ion at m/z 259 and the 4-substituted hydroxyphenylthio ion are the main fragments of the second pathway of the rearranged parent ions of compounds **9, 10** and **11**. Splitting of the sulfide ion produces a nitroso-4-nitrophenylthio ion at m/z 182 and an aryl ion, while its degradation gives three daughter ions at m/z 229, 171 and 139 respectively, due to the successive loss of NO, CNO_2 and S radicals[18]. The 3-substituted phenol ion is found to be the sole fragment of the 4-substituted hydroxyphenylthio ion.

The dinitrophenylthio bond cleavage produces the last decomposition route for the bromo-and chloro-derivatives **12** and **13** giving a 4-substituted phenyl dinitrophenylsulfide ion and a 4-substituted phenylthio ion. Elimination of the substituent R and a molecule of hydrogen from the earlier ion produce a dini-



SCHEME 3

trophenylthiocarbazole ion at m/z 272. Further depletion of S and two nitro groups lead to the formation of a dinitrobiphenylene ion and later to a biphenylene ion at m/z 240 and 148 respectively. The two phenylthio and phenyl ions at m/z 108 and 76 are further fragments of the 4-substituted phenylthio ion due to the successive loss of R and S radicals.

The oxidation of compounds **(1–6)** either by 30% H_2O_2 or $KMnO_4$ in glacial acetic acid failed to produce the corresponding sulfones. This is probably due to the fact that arylthio ring being flanked by two nitro groups which inhibit the oxidation process. This decrease in reactivity may be attributed both to the repulsion between the oxidising reagent and the negatively polarized nitro-oxygen atoms, in addition to the shielding of the sulfur reaction center by attractive sulfur-**(II)**-oxygen (nitro) interaction in the initial state[26]. On the other hand, the *bis* arylthio compounds **(9–13)** undergo oxidation by $KMnO_4$ in glacial acetic acid to give the corresponding 1,2-*bis*-arylsulfonyl-3,5-dinitrobenzenes **(15–19)**, as identified from their elemental analyses and tandem mass spectra as well as ^1H NMR spectra.

The structure proof of *bis*-arylsulfonyl compounds **(15–19)** is achieved by the ^1H NMR spectra which showed appropriate integrals, with minor but important differences. The expected chemical shifts for all protons are given in Table III.

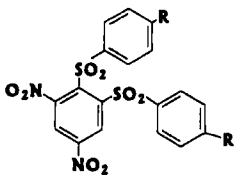
The ^1H NMR of compounds **(15–19)** showed two doublets at low (δ 9.20–9.44 ppm) and high fields (δ 8.42–8.58 ppm). A group of peaks at intermediate fields (δ 6.73–8.09 ppm) were estimated to represent the aromatic protons of the aryl sulfonyl rings.

Comparison with compounds **(1–6)** and **(9–13)** and PC permitted assignment of the two lower field peaks. Thus, the doublet at δ 9.20–9.44 ppm belongs to H-6 and represents one of the highest shift even observed for aromatic protons[25]. While the doublet at δ 8.42–8.58 ppm is assigned to the proton located between the two nitro groups at positions 3 and 5. As in compounds **(9–13)** the ^1H NMR of the methyl and methoxy protons of the two arylsulfonyl moieties in com-

TABLE III ^1H NMR data of 1,2-bis-arylsulfonyl-2,5-dinitrobenzenes (15–19)

Cpd	*R*	δ *ppm. (DMSO-d_6)*					
		H-4[a] (d)	H-6[b] (d)	H-2′,6′ (d)	H-2″,6″ (d)	H-3′,5′ (d)	H-3″,5″ (d)
15	H	9.39	8.49	8.09	7.57	7.16	6.73
16	CH_3[a]	9.35	8.46	7.90	7.35	7.18	7.11
17	OCH_3[b]	9.20	8.42	8.06	7.14		6.75(m)
18	Br	9.44	8.55	7.92	7.72	7.38	6.92
19	Cl	9.40	8.58	7.98	7.57	7.28	7.03

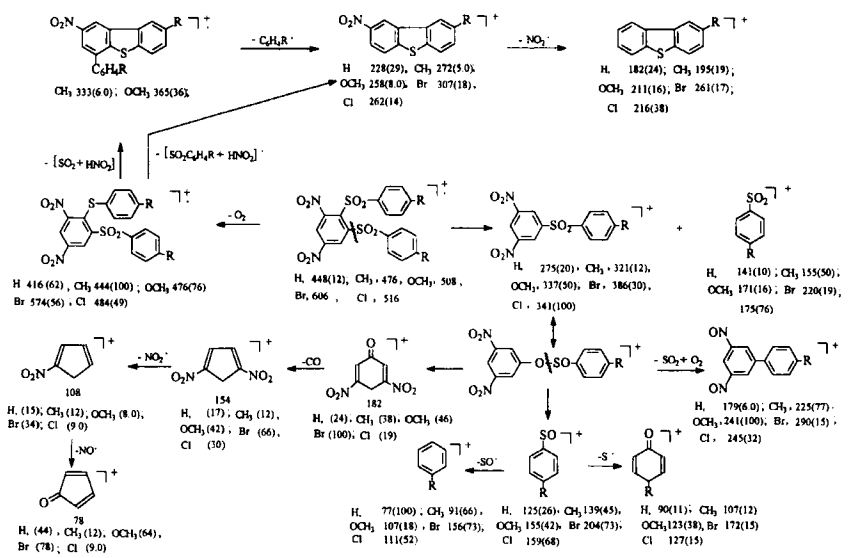
[a] 4′-CH_3 protons appear at δ 2.45 and 2.28 ppm
[b] 4′-OCH_3 protons appear at δ 3.88 and 3.72 ppm.



15-19
15, R = H; 16, R = CH_3; 17, R = OCH_3;
18, R = Br; 19, R = Cl

pounds (**16**) and (**17**) respectively resonate at two different positions. This results in two sets of signals starting at high fields: the singlet at δ 2.45 ppm and 3.88 ppm for compounds (**16**) and (**17**) respectively can be assigned to methyl and methoxy protons of the arylsulfonyl group attached to C-1 while the other singlet at δ 2.28 and 3.72 ppm is assigned to methyl and methoxy protons of arylsulfonyl group attached to C-2.

Scheme 4 adequately explains the two main fragmentation pathways of the disulfones (**15–19**) which do not show molecular ion peaks except (**15**, R = H). Whereby ejection of a molecule of oxygen directs the first dissociation route giving rise to an arylthiosulfone fragment (**16**, R = CH_3, base peak). This splits further to produce a substituted nitrothiocarbazole ion via depletion of an arylsulfonyl radical and HNO_2. This ion eventually can be also obtained through gradual elimination of [SO_2 + HNO_2] displaying an arylsubstituted nitrothio-



SCHEME 4

carbazole cation, followed by loss of an aryl radical (exclusive to **16**, R = CH_3 and **17**, R = OCH_3). On the other hand, the substituted thiocarbazole ion is envisaged to arise through loss of $NO_2^{\cdot}$ from the preceeding nitro one.

Scission of the C-SO_2 bond represents the second decomposition route rendering an arylsulfonyl cation and a monosulfone fragment (**19**, R = Cl, base peak). That upon rearrangement eliminates [SO_2 + O_2] or undergoes O-SO bond cleavage to give a 4′-substituted 3,5-dinitrosobiphenyl ion (**17**, R = OCH_3, base peak), a dinitrophenoxy ion at m/z 182 (**18**, R = Br, base peak) and an aryl sulfinyl ion. Further fragmentation of the dinitrophenoxy ion produces a dinitropentadienyl ion at m/z 154, a nitropentadienyl ion at m/z 108 and a pentadieneone ion at m/z 78 following the successive loss of CO, $NO_2^{\cdot}$ and $NO^{\cdot}$. The observed aryl ion (**15**, R = H, base peak) and the substituted phenoxy ion are the expected natural fragments of the aryl sulfinyl ion.

EXPERIMENTAL

Melting points were uncorrected. Microanalyses were performed by the microanalysis unit, Faculty of Science, Alexandria University, Egypt. Infrared spectra (KBr pellets) were measured on Perkin-Elmer 1430 ratio recording infrared and the electronic spectra were recorded in ethanol on UV-VIS Shimadzu 160-A spectrometer. The ^{1}HNMR spectra were recorded on IBM 200 MHz FTNMR-spectrometer. The mass spectrometer was a Finnigan MAT TSQ 700 instrument (Louvain La Neure University, Belgium). Samples were introduced *via* direct probe from 50–200°C. The electron energy was 70 eV.

Preparation of 2-Chloro-1,3,5-trinitrobenzene[27] (Picryl chloride)

1-Chloro-2,4-dinitrobenzene (20.1 g, 0.1 mole) in concentrated sulfuric acid (200 ml) and fuming nitric acid (100 ml, d: 1.51) were heated at 140°C for 17 hours. The reaction-mixture was then cooled and poured into ice-water. The product was recrystallized twice from methanol as yellow plates.

Synthesis of 2-arylthio-1,3,5-trinitrobenzene (1–6)

An ethanolic solution of the appropriate sodium arylthiolate (0.006 mole arylthiol and 0.004 sodium in 10 ml ethanol) was added to the stirred ethanolic solution of 2-chloro-1,3,5-trinitrobenzene (picryl chloride, 0.004 mole) at room temperature. An immediate yellow precipitate is formed and the reaction mix-

ture was poured onto cooled 5% NaOH solution. The product was filtered, washed well with water and dried. All the separated 2-arylthio-1,3,5-trinitrobenzenes in quantitative yield were crystallized from MeOH or benzene as yellow needles or plates. The ^{1}H NMR data are given in Table I.

2-Phenylthio-1,3,5-Trinitrobenzene (1)

Yellow needles, yield 95%, m.p. 97°C. UV (EtOH): λ_{max} nm = 210 (ϵ = 10281). IR (KBr) ν cm^{-1}: 1595 (aromatic C=C), 1546 and 1345 (asym and sym NO_2), 688 (C-S). Anal. Calcd for: $C_{12}H_7N_3O_6S$: C, 44.86; H, 2.18; N, 13.08; S, 9.97. Found: C, 44.52; H, 2,31; N, 12.94; S, 9.63. MS: 321 (M^+).

2-(4'-Methylphenylthio)-1,3,5-trinitrobenzene (2)

Yellow plates, yield 95% m.p. 148–50°C. UV (EtOH): λ_{max} nm = 210 (ϵ = 7135). IR (KBr) ν cm^{-1}: 1596 (aromatic C=C), 1545 and 1339 (asym and sym NO_2), 698 (C-S). Anal. Calcd for $C_{13}H_9N_3O_6S$: C, 46.57; H, 2.69; N, 12.54; S, 9.55. Found: C, 46.37; H, 2.78; N, 12.32; S, 9.14. MS: 335 (M^+).

2-(4'-Methoxyphenylthio)-1,3,5-trinitrobenzene (3)

Yellow plates, yield 97%, m.p. 109–50°C. UV (EtOH): λ_{max} nm = 210 (ϵ = 7136). IR (KBr) ν cm^{-1}: 1592 (aromatic C=C), 1547 and 1344 (asym and sym.NO_2), 653 (C-S). Anal. Calcd for $C_{13}H_9O_7S$: C, 44.44; H, 2.56; N, 11.96; S, 9.12. Found: C, 44.65; H, 2.68; N, 12.21; S, 9.35. MS: 351 (M^+).

2-(4'-Bromophenylthio)-1,3,5-trinitrobenzene (4)

Yellow needles, yield 90%, m.p. 133°C. UV (EtOH): λ_{max} nm = 207 (ϵ = 5540). IR (KBr) ν cm^{-1}: 1595 (aromatic C=C), 1541 and 1342 (asym and sym.NO_2), 651 (C-S). Anal. Calcd for $C_{12}H_6BrN_3O_6$: C, 36.00; H, 1.50; N, 10.50; S, 8.00. Found: C, 36.23; H, 1.35; N, 10.73; S, 7.88. MS: 400 (M^+).

2-(4'-Chlorophenylthio)-1,3,5-trinitrobenzene (5)

Yellow needles, yield 88%, m.p. 113–4°C. UV (EtOH): λ_{max} nm = 212 (ϵ = 8055). IR (KBr) ν cm^{-1}: 1595 (aromatic C=C), 1542 and 1342 (asym and sym.NO_2), 651 (C-S). Anal. Calcd for $C_{12}H_6ClN_3O_6S$: C, 40.56; H, 1.69; N, 11.83; S, 9.01. Found: C, 40.18; H, 1.78; N, 11.92; S, 8.89. MS: 355.5 (M^+).

2-(4′-Nitrophenylthio)-1,3,5-trinitrobenzene (6)

Yellow needles, yield 85%, m.p. 143°C. UV (EtOH): λ_{max} nm = 214 (ϵ = 8140). IR (KBr) ν cm^{-1}: 1595 (aromatic C=C), 1545 and 1342 (asym and sym.NO_2), 650 (C-S). Anal. Calcd for $C_{12}H_6N_4O_8S$: C, 39.34; H, 1.64; N, 15.30; S, 8.74. Found: C, 39.55; H, 1.83; N, 15.22; S, 8.34. MS: 366 (M^+).

Synthesis of 1,2-bis-arylthio-2,5-dinitrobenzenes (9–13)

An ethanolic solution 2-chloro-1,3,5-trinitrobenzene (0.004 mole) was treated with the appropriate 0.008 mole sodium arylthiolate (prepared by 0.01 mole arylthiol and 0.008 mole sodium in 5 ml ethanol) at room temperature with stirring. A precipitate is formed immediately with deep brown solution. On work up the *bis* arylthio compounds **(9–13)** were obtained in a quantitative yield. All the separated *bis* arylthio compounds were crystallized from MeOH or benzene as yellow needles or plates. The ^1H NMR data are given in Table II.

1,2-bis-(Phenylthio)-3,5-dinitrobenzene (9)

Yellow needles, yield 94%, m.p. 125°C. UV (EtOH): λ_{max} nm = 210 (ϵ = 41800), IR (KBr) ν cm^{-1}: 1591 (aromatic C=C), 1526 and 1358 (asym and sym.NO_2), 663 (C-S). Anal. Calcd for $C_{18}H_{12}N_2O_4S_2$: C, 56.25; H, 3.12; N, 7.29; S, 16.66. Found: C, 56.41; H, 3.17; N, 7.13; S, 17.07. MS: 384 (M^+).

1,2-bis-(4′-Methyphenylthio)-3,5-dinitrobenzene (10)

Yellow needles, yield 95%, m.p. 133–4°C. UV (EtOH): λ_{max} nm = 208 (ϵ = 35360); IR (KBr) ν cm^{-1}: 1588 (aromatic C=C), 1520 and 1335 (asym and sym. NO_2), 663 (C-S). Anal. Calcd for $C_{20}H_{16}N_2O_4S_2$: C, 58.25; H, 3.88; N, 7.79; S, 15.53. Found: C, 58.59; H, 3.85; N, 6.64; S, 15.31. MS: 412 (M^+).

1,2-bis-(4′-Methoxyphenylthio)-3,5-dinitrobenzene (11)

Yellow needles, yield 95%, m.p. 93–5°C. UV (EtOH): λ_{max} nm = 206 (ϵ = 33580); IR (KBr) ν cm^{-1}: 1590 (aromatic C=C), 1526 and 1340 (asym and sym. NO_2), 662 (C-S). Anal. Calcd for $C_{20}H_{16}N_2O_6S_2$: C, 54.05; H, 3.60; N, 6.31; S, 14.41 Found: C, 54.41; H, 3.40; N, 7.68; S, 14.19. MS: 444 (M^+).

1,2-bis-(4'-Bromophenylthio)-3,5-dinitrobenzene (12)

Yellow needles, 90%, m.p. 84°C. UV (EtOH): λ_{max} nm = 209 (ϵ = 37260). IR (KBr) ν cm^{-1}: 1593 (aromatic C=C), 1529 and 1339 (asym and sym.NO_2), 662 (C-S). Anal. Calcd for $C_{18}H_{10}Br_2N_2O_4S_2$: C, 39.85; H, 1.84; N, 5.17; S, 11.81 Found: C, 39.95; H, 1.75; N, 5.54; S, 11.74. MS: 542 (M^+).

1,2-bis-(4'-Chlorophenylthio)-3,5-dinitrobenzene (13)

Yellow needles, yield 90%, m.p. 78–80°C. UV (EtOH): λ_{max} nm = 207 (ϵ = 29840). IR (KBr) ν cm^{-1}: 1589 (aromatic C=C); 1541 and 1340 (asym and sym.NO_2), 662 (C-S). Anal. Calcd for $C_{18}H_{10}Br_2N_2O_4S_2$: C, 47.79; H, 2.21; N, 6.19; S, 14.16 Found: C, 47.42; H, 2.22; N, 6.24; S, 14.31. MS: 452 (M^+).

Synthesis of 1,2-bis-arylsulfonyl-3,5-dinitrobenzenes[28] (15–19)

Each *bis*-sulfide (0.01 mole) was dissolved in just enough glacial acetic acid to put it into solution. In cases of difficulty soluble sulfides solution may be facilitated by gentle warming. The solution was treated with 50% excess of the calculated amount of potassium permenganate dissolved in thirty times its weight of water to form the sulfone. The permenganate was added, with shaking, as fast it was decolorized. When all permenganate had been added, two or three volume of crashed ice is added. The precipitate is filtered, dried and recrystallized from methanol-benzene as yellow crystals. The ^1H NMR data are given in Table III.

1,2-bis-(Phenylsulfonyl)-3,5-dinitrobenzene (15)

Yellow crystals, yield 70%, m.p. 205–7°C. UV (EtOH): λ_{max} nm = 239 (ϵ = 15940). IR (KBr) ν cm^{-1}: 1580 (aromatic C=C), 1543 and 1345 (NO_2 asym and sym respectively), 1317 and 1148 (SO_2 sym and asym respectively). Anal. Calcd for $C_{18}H_{12}N_2S_2O_8$: C, 48.21; H, 2.68; N, 6.25; S, 14.28. Found: C, 48.61; H, 2.84; N, 6.51; S, 14.33. MS: 448 (M^+).

1,2-bis-(4'-Methylphenylsulfonyl)-3,5-dinitrobenzene (16)

Yellow plates, yield 75%, m.p. 148–150°C. UV (EtOH): λ_{max} nm = 238 (ϵ = 20500). IR (KBr) ν cm^{-1}: 1590 (aromatic C=C); 1530 and 1341 (NO_2 asym and sym respectively), 1310, 1146 (SO_2 sym and asym respectively). Anal.

Calcd for $C_{20}H_{16}N_2S_2O_8$: C, 50.42; H, 3.36; N, 5.88; S, 13.44. Found: C, 50.13; H, 3.52; N, 5.41; S, 13.63. MS: 476 (M^+).

1,2-bis-(4′-Methoxyphenylsulfonyl)-3,5-dinitrobenzene (17)

Yellow plates, yield 75%, m.p. 173–5°C. UV (EtOH): λ_{max} nm = 250 (ϵ = 23800); 361 (ϵ = 4640). IR (KBr) ν cm^{-1}: 1590 (aromatic C=C), 1545 and 1343 (NO_2 asym and sym respectively), 1305 and 1139 (SO_2 sym and asym respectively). Anal. Calcd for $C_{20}H_{16}N_2S_2O_{10}$: C, 47.24; H, 3.15; N, 5.51; S, 12.59. Found: C, 47.50; H, 3.16; N, 5.63; S, 12.71. MS: 508 (M^+).

1,2-bis-(4′-Bromophenylsulfonyl)-3,5-dinitrobenzene (18)

Yellow needles, yield 80%, m.p. 183–5°C. UV (EtOH): λ_{max} nm = 244 (ϵ = 21760); 346 (ϵ = 4080). IR (KBr) ν cm^{-1}: 1592 (aromatic C=C); 1533 and 1341 (NO_2 asym and sym respectively), 1347 and 1139 (SO_2 sym and asym respectively). Anal. Calcd for $C_{18}H_{10}Br_2N_2O_8S_2$: C, 35.64; H, 1.65; N, 4.62; S, 10.56. Found: C, 35.74, H, 1.47; N, 4.56; S, 10.71. MS: 605.40 (M^+).

1,2-bis-(4′-Chlorophenylsulfonyl)-3,5-dinitrobenzene (19)

Yellow needles, yield 80%, m.p. 175–7°C. UV (EtOH): λ_{max} nm = 244 (ϵ = 24320); 346 (ϵ = 4820). IR (KBr) ν cm^{-1}: 1585 (aromatic C=C); 1534 and 1534 (NO_2 asym and sym respectively), 1348 and 1139 (SO_2 sym and asym respectively). Anal. Calcd for $C_{18}H_{10}Cl_2N_2O_8S_2$: C, 44.86; H, 1.94; N, 5.42; S, 12.40. Found: C, 44.59, H, 1.78; N, 5.52; S, 12.31. MS: 516 (M^+).

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