1,2,3-Thiadiazole Derivatives with a Nearly Linear N-S...O Grouping. X-Ray Crystal Structure Analysis of Four Methylated Products of 4-Phenyl-1,2,3-thiadiazole-5-carbaldoxime

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The title oxime **6** was methylated under different conditions and yielded four monomethylated products **7-10** and two bismethylated products **11** and **12** which were easily distinguished by their ^{13}C nmr spectra. In view of the potential thiapentalene character of **8**, **9**, **10** and **11**, their X-ray crystal structures were determined. The structural properties of the nitroso compound **9** are in accordance with a thiapentalene structure, whereas those of the other compounds deviate in the order **10** < **11** << **8**.

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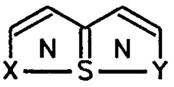
The question of the nature of bonding in 6aλ^4-thiapentalenes has motivated numerous experimental and theoretical studies since 1958 when the first X-ray crystal structure was reported [1,2]. These molecules of general structure **1** have a nearly linear arrangement of the X-S-Y unit, with bond lengths that are longer than covalent bonds, but much shorter than the sum of the atomic van der Waals radii [3]. They are usually described by the dual canonical forms **1A** and **1B** which indicate single bond/no bond resonance.



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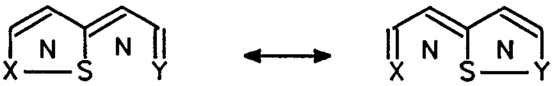
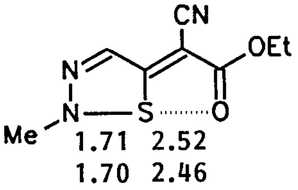


1A **1B**

When X = S or NR and Y = O, the sulfur-oxygen distance in most cases ranges between 2.0 and 2.5 Å [3], substantially greater than the covalent bond length of 1.70 Å, but well below the van der Waals separation of 3.2 Å. Hence, canonical form **1A** (X = S or NR, Y = O) is the major resonance contributor to the structure of such molecules. A lower limit of about 1.85 Å for S-O distances is provided by symmetrical 1,6-dioxa-6aλ^4-thiapentalenes **1** (X = Y = O) [4], where the two resonance forms **1A** and **1B** contribute equally to the overall structure.

In the field of 1,2,3-thiadiazoles the X-ray crystal structure of **2** has been determined [5]. Here, there are two crystallographically independent molecules in the crystal unit, each with a nearly linear N-S...O sequence, and with essentially normal S-N bond lengths of 1.71 and 1.70 Å, and weak S...O contacts of 2.52 and 2.46 Å. Also, two mesoionic thiadiazoles **3** and **4** have been reported which show some degree of S...O interaction [5,6].



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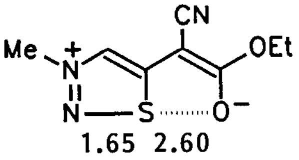

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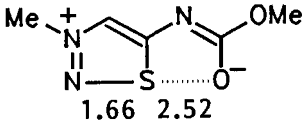

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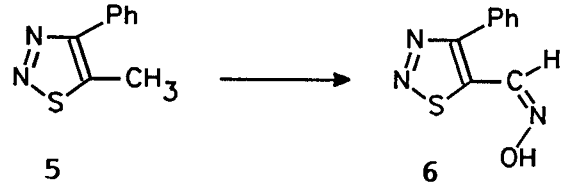
In continuation of our studies on thiapentalenic systems derived from 1,2,3-thiadiazole-5-carbaldehyde [7], we have now investigated the methylation products of 4-phenyl-1,2,3-thiadiazole-5-carbaldoxime and determined the molecular structures of four derivatives.

The aldoxime **6** was readily prepared by nitrosation of 5-methyl-4-phenyl-1,2,3-thiadiazole **5** with isoamyl nitrite in the presence of potassium ethoxide, and was identified as the Z-isomer on the basis of the ^{13}C nmr spectrum. Indeed, the C5 carbon resonance at δ 133.7 is shifted upfield by *ca* 13 ppm compared with that of the corresponding aldehyde (δ 147.1) [7] due to a combination of the substituent (*ca* 4 ppm) and γ-effects (*ca* 10 ppm) [8]. The large imine $^1J_{CH}$ coupling constant of 186 Hz also supports this conclusion [9].

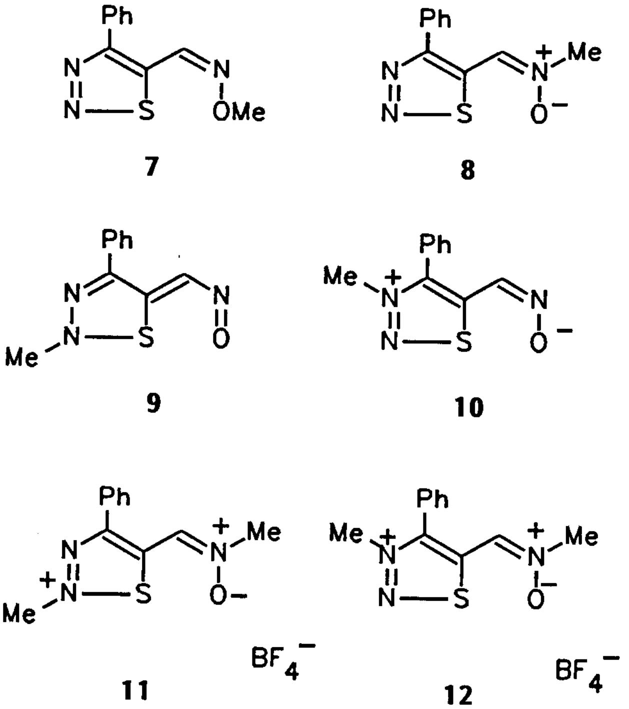


5 6

Scheme 1 lists the structures of the methylated products obtained from **6** under a variety of conditions. Thus, with an excess of diazomethane in ether at room temperature, the oxime ether **7** and the nitrone **8** were obtained as the sole reaction products in 59 and 24% yield after chromatographic separation. According to the nmr spectrum of the crude reaction mixture, 78% of **7** (δ 4.2) and 22% of **8** (δ 4.05) were present. The same products, but in reverse proportions (ratio 1:4 by nmr), were obtained when the potassium salt of **6** was heated with a tenfold excess of methyl iodide in acetonitrile.

When the methylation of **6** was carried out with two equivalents of Meerwein's reagent in dichloromethane, the nitrone **8** was the major product (20%), along with two bismethylated products, **11** (5%) and **12** (11%). The *O*-trimethylsilylated derivative of **6** was also subjected to Meerwein's reagent and then desilylated with potassium fluoride, giving again **8** as major product (40%) but now accompanied by the ring methylated derivatives **9** and **10** in 8-9% yield. The ratio of the products **8**:**9**:**10**, determined by nmr of the crude reaction mixture, was 54:19:27%.

Scheme 1



7 8 9 10 11 12

The structures of the reaction products were established essentially on the basis of their nmr spectra (Table 1). Thus, **7** and **8** show intact thiadiazole rings with C4 absorptions at the same position as in **6** (δ 160-162). In the other methylated compounds **9-12** this carbon atom absorption has shifted upfield by 5-15 ppm. Products **7** and **8** are easily differentiated by a consideration of the chemical shift of the methyl carbon atoms: δ 63.3 for **7** and δ 51.4 for **8**, the latter absorbing as a double quartet due to coupling with the CH=N proton ($^3J_{CH}$ = 2.2 Hz). Note also that the C5 resonance of **7** (δ 134) occurs at the same position as in **6**, suggesting a Z-configuration.

Table 1

^{13}C Chemical Shifts of the Heterocycles [a]

Compound	Solvent	C4	C5 ($^2J_{CH}$)	CHN ($^1J_{CH}$)	CH$_3$ ($^1J_{CH}$)
6	$(CD_3)_2SO$	160.7	133.7 (12)	135.9 (186)	
7	$CDCl_3$	162.1	133.9 (10)	136.1 (186)	63.3 (145.6)
8	$(CD_3)_2SO$	159.7	137.5 (9)	128.9 (195)	51.4 (143.3)
9	$CDCl_3$	148.6	135.7 (14.5)	140.7 (193)	38.5 (141.7)
10	$CDCl_3$	145.3	141.8 (14)	138.6 (191)	44.0 (143)
11	$(CD_3)_2SO$	155.8	142.5 (11)	133.8 (202)	43.6 and 50.0 (146 and 145)
12	$(CD_3)_2SO$	153.5	148.1 (10)	130.6 (200)	45.6 and 51.0 (147 and 144.5)

[a] The phenyl carbon atoms absorb in the region δ 128.5-132, except the ipso carbon atoms of **10** (δ 126.8) and **12** (δ 124.0).

In **9** and **10** methylation has occurred at the thiadiazole ring since their C4 carbon absorptions (δ 148/145) have shifted upfield considerably compared with **6**, indicating a structural variation of the ring skeleton. The compound with highest chemical shift (δ 44) and highest $^1J_{CH}$ coupling constant (143 Hz) for the methyl substituent is assigned the mesoionic structure **10** [7]. This is further corroborated by the observed γ-effect of the methyl group in **10** on the ipso carbon resonance of the phenyl group; δ 126.8 compared with δ 132.3 for **9**.

This γ-effect is also present in **12** where the phenyl ipso carbon (δ 124) absorbs at higher field than in **11** (δ 128.5). The two bismethylated products were further distinguished by the multiplicity of the phenyl proton absorptions in the 400 MHz ^{1}H nmr spectra; two multiplets for **11** and a quasi singlet for **12**. Thus, steric hindrance between the methyl and phenyl groups in **12** forces the phenyl group to rotate out of the plane of the heterocycle, resulting in a singlet absorption.

The compounds **8-12** are potential candidates for a thiapentalene structure **1**, characterized by the presence of a hypervalent sulfur connected to two electronegative atoms X and Y in a linear (or nearly linear) arrangement [3]. We have selected four compounds for our X-ray crystallographic analysis and the results are shown in Figures 1-4. They all show N-S-O angles within 13° of colinearity.

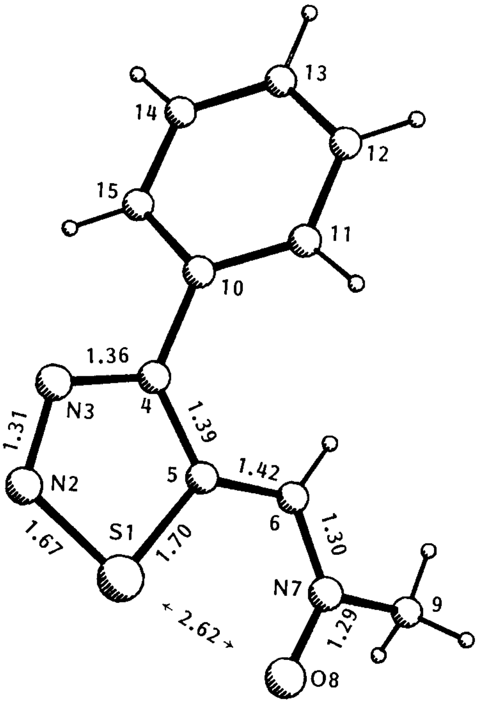


Figure 1. Molecular structure of **8** with numbering scheme and selected bond lengths.

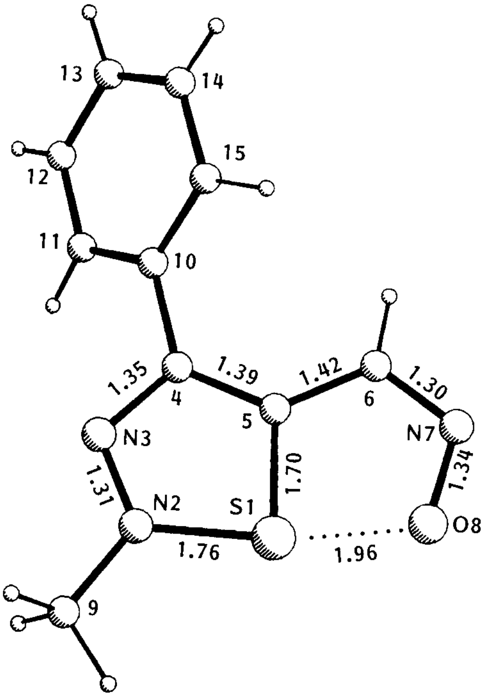


Figure 2. Molecular structure of **9** with numbering scheme and selected bond lengths.

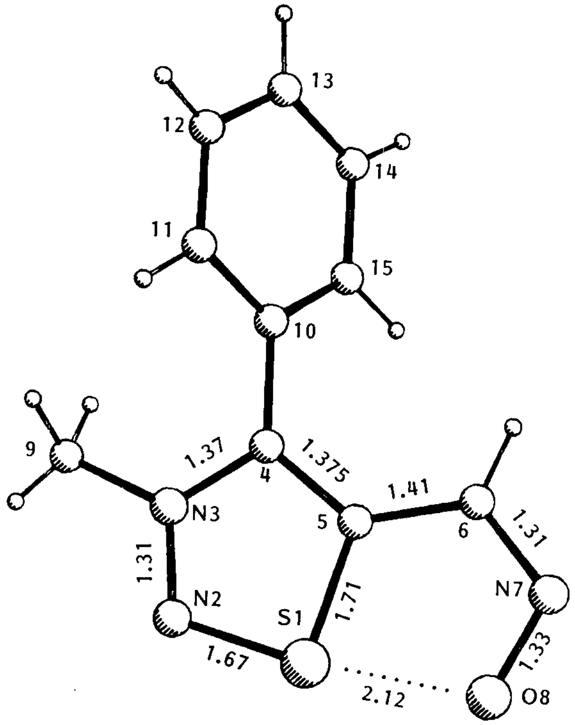


Figure 3. Molecular structure of **10** with numbering scheme and selected bond lengths.

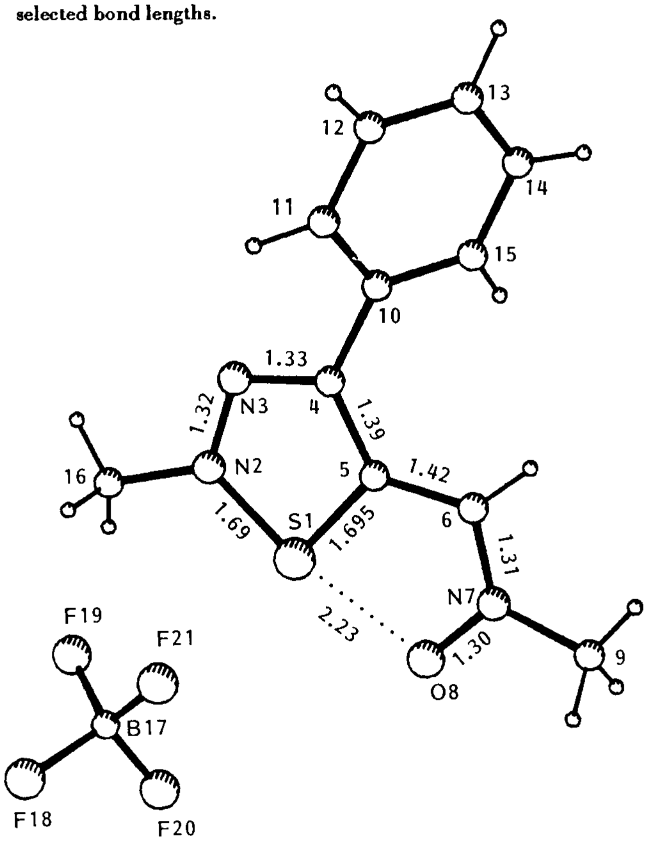


Figure 4. Molecular structure of **11** with numbering scheme and selected bond lengths.

When the phenyl group is left out of consideration, the heterocycles **9** and **10** are planar with a maximum deviation from the best plane through the eight atoms 1-8 of 0.013 and 0.018 Å respectively. The deviations in **11** are more pronounced (0.042 Å), and in **8** the N7 atom is 0.075 Å from the best plane. In all cases the nitrogen atoms are sp^2; the greatest deviation is found for N7 in **11** which lies only 0.026 Å out of the plane through its neighbors C6, O8 and C9.

The S1-N2 bond lengths in **8** and **10** (1.67 Å) are normal for thiadiazoles [10] and the lengthening of S1-N2 in **9** (1.76 Å) is about what would be expected when a two-coordinated nitrogen is replaced by a three-coordinated nitrogen atom [11]. The transformation of **9** into the cation **11** is accompanied by a marked shortening of the S1-N2 bond (1.69 Å).

Table 2

Atomic Coordinates (x 10^4) and Equivalent Temperature Factors ($Å^2$)(x 10^3), (S1 x 10^4) of Compound **8**

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$

	x	y	z	Ueq
S1	7894(1)	5054(1)	1376(1)	416(3)
N2	6873(3)	4125(1)	466(2)	48(1)
N3	6593(3)	4311(1)	-861(2)	42(1)
C4	7182(3)	5218(2)	-1183(2)	32(1)
C5	8010(3)	5742(2)	-54(2)	31(1)
C6	8956(3)	6647(2)	-70(2)	34(1)
N7	9717(2)	7043(1)	1076(2)	38(1)
O8	9551(2)	6680(1)	2267(1)	48(1)
C9	10821(4)	7922(2)	1070(3)	56(1)
C10	6911(3)	5562(2)	-2628(2)	32(1)
C11	6093(3)	6462(2)	-2977(2)	39(1)
C12	5837(3)	6786(2)	-4336(3)	45(1)
C13	6410(3)	6211(2)	-5343(2)	49(1)
C14	7216(4)	5324(2)	-5003(2)	52(1)
C15	7469(3)	4986(2)	-3656(2)	42(1)

All four compounds have S...O distances shorter than the sum of the corresponding van der Waals radii (3.2 Å). The closest S...O distance is found in the nitroso derivative **9**, 1.96 Å; a value similar to that of a reported thiapentalene analogue with S-S...O structural unit (2.03 Å) [12]. These are the shortest S...O distances found for non-symmetrical thiapentalenes **1** (X $\neq$ O, Y = O), and they approach the value of 1.85 Å for 1,6,6aλ^4-dioxathiapentalenes **1** (X = Y = O). The S...O distances in **10** and **11** are also relatively short, but that of **8** is much longer.

In order to estimate the covalent bond strength of S1...O8, Huggins' equation (1) can be used [13]:

$$D_{AB} = 10^{2(r_A^* + r_B^* - r_{AB})} \qquad (1)$$

Table 3

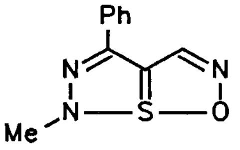
Atomic Coordinates (x 10^4) and Equivalent Temperature Factors ($Å^2$)(x 10^3) of Compound **9**

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$

	x	y	z	Ueq
S1	1163(2)	6350(1)	4581(1)	46(1)
N2	710(5)	5907(3)	3936(1)	44(1)
N3	620(5)	6826(3)	3592(1)	42(1)
C4	900(5)	7964(4)	3824(2)	38(1)
C5	1203(5)	7877(4)	4355(2)	37(1)
C6	1567(6)	8820(5)	4737(2)	47(1)
N7	1848(6)	8430(4)	5210(2)	61(2)
O8	1722(5)	7159(4)	5249(1)	65(1)
C9	353(7)	4598(4)	3780(2)	53(2)
C10	850(5)	9135(4)	3506(2)	40(1)
C11	1647(7)	9179(5)	3023(2)	52(2)
C12	1581(8)	10270(6)	2729(2)	68(2)
C13	724(9)	11339(6)	2915(3)	77(2)
C14	-62(8)	11317(5)	3387(2)	67(2)
C15	-11(7)	10226(4)	3694(2)	50(2)

where D_{AB} is the bond dissociation energy in kcal/mole, r_{AB} is the observed bond distance, and r_A^* and r_B^* are the computed constant energy radii for the atoms A and B. In the case of **8**, the S1...O8 distance is larger than the Huggins constant energy distance of 2.58 Å, indicating no covalent bonding but rather a weakly interacting contact. The same conclusion should be drawn for the reported compounds **2-4**. In **9**, and also to a much lesser extend in **10** and **11**, S-O bonding exists and the calculated dissociation energies are 17, 8 and 5 kcal/mole respectively. It is also noteworthy that in **9** and **10** the nitroso N-O bonds are lengthened (1.34 and 1.33 Å), and the angles C6-N7-O8 reduced (112°) compared with those in **8** and **11** (1.29 and 1.30 Å, 122 and 119.5°).

From all these results we conclude that the nitrone **8** has no thiapentalene characteristics, and that those of the methylated nitrone **11** are poor. On the contrary, structure **13** is an acceptable representation of molecule **9**, and **14** may also be considered as contributing to the structure of **10**.



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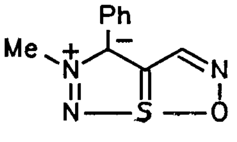

14

EXPERIMENTAL

4-Phenyl-1,2,3-thiadiazole-5-carbaldoxime (**6**).

To a solution of potassium (4 g) in absolute ethanol/ether (17/25 ml) was added at −5° isoamyl nitrite (6.5 g, 55 mmoles) and **5** (9 g, 50 mmoles) and the whole was stirred at room temperature for 1 day. The precipitated yellow potassium salt was dissolved in water and acidified with aqueous hydrochloric acid (2*N*) to *p*H 3.0. The precipitate was filtered off, washed with *n*-hexane and crystallized from ethanol/water to give beige needles of **6** in 49% yield (5.06 g), mp 212°; ^{1}H nmr (250 MHz, dimethyl sulfoxide-d$_6$): δ 7.5-7.9 (two m, 5H, Ph), 8.1 (s, 1H, CH = N), 13.7 (s, 1H, OH); ^{13}C nmr: see Table 1; ms: (%) m/z 205 (16, $M^{+\cdot}$), 150 (83), 121 (58, PhCS$^+$), 105 (100), 89 (78), 77 (55, Ph$^+$).

Anal. Calcd. for $C_9H_7N_3OS$ (mol wt 205): C, 52.67; H, 3.44. Found: C, 52.51; H, 3.33.

Methylation of Oxime 6.

A. With Diazomethane.

To a suspension of **6** (2 g, 9.75 mmoles) in dry diethyl ether (50 ml) was added a threefold excess of diazomethane (*ca* 2 g), dissolved in diethyl ether (70 ml) [14], and the mixture was stirred overnight at room temperature. After evaporation of the solvent, the residue was chromatographed on silica gel first with diethyl ether/light petroleum (2:1) and then with diethyl ether/methanol (10:1) as the eluents. The first fraction gave **7** in 58.5% yield (1.25 g) and the second fraction gave **8** in 23% yield (0.5 g).

B. With Methyl Iodide.

To a suspension of the potassium salt of the oxime **6** (0.7 g, 2.9 mmoles) in acetonitrile (30 ml) was added ten equivalents of methyl iodide (4.2 g), and the mixture was refluxed for 90 minutes. After evaporation of the solvent and the excess of methyl iodide, the residue was chromatographed on silica gel with chloroform/methanol (5:1) as the eluent to give impure **7** (70 mg) and **8** in 42.5% yield (270 mg).

C. With Meerwein's Reagent.

A mixture of **6** (3 g, 15 mmoles) and trimethyloxonium tetrafluoroborate (4.4 g, 30 mmoles) in dry dichloromethane (50 ml) was stirred at room temperature for 2 days, and then treated with aqueous sodium bicarbonate (2.5 g in 100 ml). The dichloromethane layer was separated from the aqueous layer and the latter was extracted three times with chloroform. During this extraction **11** precipitated in 5% yield (244 mg). The combined organic layers were dried over magnesium sulfate and evaporated to give a mixture of **8** and **12** in a ratio of 3:1 by nmr. This mixture was allowed to crystallize from chloroform/hexane at room temperature, yielding **12** in 11% yield (535 mg). The filtrate was evaporated and the residue triturated with methanol to give **8** in 20% yield (670 mg).

In another experiment the oxime **6** (3.075 g, 15 mmoles) was stirred with trimethylsilyl chloride (1.8 g, 16.5 mmoles) and triethylamine (1.5 mg, 16.5 mmoles) in dichloromethane (100 ml) at room temperature of 15 minutes. After removal of the solvent, the residue was extracted with diethyl ether (60 ml) and the filtered extract evaporated to give the silylated oxime. This compound was dissolved in dichloromethane (50 ml) and allowed to react overnight with trimethyloxonium tetrafluoroborate (2.44 g, 16.5 mmoles). The solvent was evaporated and the residue was dissolved in methanol (60 ml) and treated with aqueous potassium fluoride (2 g in 100 ml). The mixture was extracted three times with dichloromethane (100 ml) and the combined organic layers were dried over magnesium sulfate, evaporated, and chromatographed on silica gel with diethyl ether/methanol (first 1:0, then 5:1) as the eluent. Three fractions were collected composed of a mixture of **6** and **9** (first fraction), **8** (1.3 g, 40%) and **10** (304 mg, 9%). The first fraction was further chromatographed with diethyl ether/light petroleum (2:1) as the eluent, giving **6** (315 mg) and **9** (270 mg, 8%).

5-(Methoxyiminomethyl)-4-phenyl-1,2,3-thiadiazole (7).

This compound crystallized from diethyl ether/*n*-hexane as pale yellow crystals, mp 48°; ^{1}H nmr (400 MHz, deuteriochloroform): δ 4.2 (s, 3H, OMe), 7.5-7.8 (two m, 5H, Ph), 7.94 (s, 1H, CH = N); ^{13}C nmr: see Table 1; ms: (%) m/z 219 (21, $M^{+\cdot}$), 164 (41), 134 (38, PhC ≡ CSH$^{+\cdot}$), 121 (28, PhCS$^+$), 105 (100), 91 (47), 89 (56), 77 (39, Ph$^+$).

Anal. Calcd. for $C_{10}H_9N_3OS$ (mol wt 219): C, 54.78; H, 4.14. Found: C, 54.70; H, 4.07.

5-[Methyl(oxido)iminomethyl]-4-phenyl-1,2,3-thiadiazole (8).

This compound crystallized from ethanol as white crystals, mp 150°; ^{1}H nmr (400 MHz, dimethyl sulfoxide-d$_6$): δ 4.05 (s, 3H, NMe), 7.5-7.9 (m and d, 5H, Ph), 8.9 (s, 1H, CH = N); ^{13}C nmr: see Table 1; ms: (%) m/z 219 (27, $M^{+\cdot}$), 191 (39, $M^{+\cdot}$-N$_2$), 150 (100), 143 (79), 142 (50, $M^{+\cdot}$-Ph), 121 (22, PhCS$^+$), 115 (49), 105 (100), 89 (35), 77 (92, Ph$^+$), 42 (94, $HC=\overset{+}{N}Me$).

Anal. Calcd. for $C_{10}H_9N_3OS$ (mol wt 219): C, 54.78; H, 4.14. Found: C, 54.73; H, 4.07.

2-Methyl-5-nitrosomethyleen-4-phenyl-1,2,3-thiadiazole (9).

This compound crystallized from ethanol as yellow crystals, mp 117°; ^{1}H nmr (400 MHz, deuteriochloroform): δ 4.1 (s, 3H, NMe), 7.5-7.9 (m and d, 5H, Ph), 9.45 (s, 1H, CH =); ^{13}C nmr: see Table 1; ms: (%) m/z 219 (100, $M^{+\cdot}$), 202 (15), 175 (13), 146 (25), 102 (16), 89 (10), 77 (15, Ph$^+$), 51 (11), 43 (44, MeN$_2^+$).

Anal. Calcd. for $C_{10}H_9N_3OS$ (mol wt 219): C, 54.78; H, 4.14. Found: C, 54.87; H, 4.15.

3-Methyl-4-phenyl-1,2,3-thiadiazolium-5-nitrosomethylide (10).

This compound crystallized from ethanol as orange crystals, mp 229° dec; ^{1}H nmr (400 MHz, deuteriochloroform): δ 4.30 (s, 3H, NMe), 7.5-7.8 (two m, 5H, Ph), 8.9 (s, 1H, CH =), ^{13}C nmr: see

Table 4

Atomic Coordinates (x 10^4) and Equivalent Temperature Factors (Å^2)(x 10^3), (S1 x 10^4) of compound 10

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$$

	x	y	z	Ueq
S1	6858(1)	-73(1)	867(1)	484(4)
N2	6261(2)	-1679(4)	1410(2)	49(1)
N3	5616(2)	-906(4)	1891(2)	39(1)
C4	5554(3)	974(4)	1882(2)	36(1)
C5	6194(3)	1670(5)	1305(2)	37(1)
C6	6379(3)	3501(5)	1047(3)	43(1)
N7	7039(3)	3789(5)	475(2)	58(1)
O8	7450(2)	2229(4)	226(2)	64(1)
C9	4953(4)	-2117(5)	2353(4)	55(2)
C10	4864(3)	1985(4)	2406(2)	36(1)
C11	5245(3)	1881(5)	3564(3)	51(1)
C12	4585(4)	2852(6)	4032(4)	66(2)
C13	3574(4)	3949(6)	3377(4)	67(2)
C14	3197(4)	4084(5)	2234(4)	61(2)
C15	3837(3)	3103(4)	1738(3)	48(1)

Table 1; ms: (%) m/z 219 (84, $M^{+\cdot}$), 188 (12), 142 (12), 115 (20), 102 (13), 91 (17), 77 (16, Ph^+), 66 (24), 51 (13), 43 (100, MeN_2^+).

Anal. Calcd. for $C_{10}H_9N_3OS$ (mol wt 219): C, 54.78; H, 4.14. Found: C, 54.50; H, 4.15.

Table 5

Atomic Coordinates (x 10^4) and Equivalent Temperature Factors ($Å^2$)(x 10^3) of compound 11

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a^*_i a^*_j \vec{a}_i \vec{a}_j$$

	x	y	z	Ueq
S1	4428(2)	765(3)	992(1)	48(1)
N2	4858(5)	-52(8)	1909(4)	76(3)
N3	4020(5)	-200(8)	2463(3)	49(2)
C4	2963(6)	339(9)	2149(4)	39(3)
C5	3012(6)	957(10)	1353(4)	42(3)
C6	2090(7)	1772(10)	873(4)	42(3)
N7	2407(6)	2296(8)	153(4)	49(2)
O8	3509(4)	2024(7)	-81(3)	57(2)
C9	1605(10)	3289(15)	-406(6)	67(4)
C10	1896(6)	280(9)	2663(4)	41(3)
C11	1986(7)	846(11)	3471(4)	50(3)
C12	986(9)	778(13)	3945(5)	62(3)
C13	-99(9)	171(13)	3640(6)	68(4)
C14	-201(7)	-375(13)	2850(5)	63(4)
C15	794(7)	-305(11)	2359(5)	49(3)
C16	6112(7)	-587(17)	2100(6)	73(4)
B17	8385(10)	1950(18)	712(7)	65(5)
F18	9324(5)	3012(8)	932(3)	99(2)
F19	8594(5)	350(8)	1033(4)	107(3)
F20	8375(7)	1858(10)	-105(4)	146(4)
F21	7369(6)	2609(10)	972(5)	163(4)

2-Methyl-5-[methyl(oxido)iminomethyl]-4-phenyl-1,2,3-thiadiazolium Tetrafluoroborate (**11**).

This compound crystalllized from ethanol as white crystals, mp 238-248° dec; ^1H nmr (400 MHz, dimethyl sulfoxide-d_6): δ 4.3 and 4.6 (two s, 6H, two NMe), 7.7-7.95 (two m, 5H, Ph), 9.85 (s, 1H, CH=N); ^{13}C nmr: see Table 1.

Anal. Calcd. for $C_{11}H_{12}BF_4N_3OS$ (mol wt 321): C, 41.15; H, 3.77. Found: C, 41.04; H, 3.63.

3-Methyl-5-[methyl(oxido)iminomethyl]-4-phenyl-1,2,3-thiadiazolium Tetrafluoroborate (**12**).

This compound crystallized from ethanol as beige crystals, mp 159-166°; ^1H nmr (400 MHz, dimethyl sulfoxide-d_6): δ 4.1 and 4.4 (two s, 6H, two NMe), 7.8 (s, 5H, Ph), 9.05 (s, 1H, CH=N); ^{13}C nmr: see Table 1.

Anal. Calcd. for $C_{11}H_{12}BF_4N_3OS$ (mol wt 321): C, 41.15; H, 3.77. Found: C, 41.08; H, 3.76.

Crystal Structure Analysis of **8**.

Compound **8** crystallized from ethanol in the space group $P2_1/c$ with a = 7.677(3), b = 13.522(3), c = 9.808(2) Å, β = 98.64(2)°, V = 1006.6(5) Å^3, Z = 4, D_x = 1.45 g cm^{-3}. Intensities from a parallelepiped crystal 0.45 x 0.45 x 0.18 mm were measured using a Huber 4-circle diffractometer with graphite monochromatized MoKα radiation (λ = 0.71069 Å). Of the 1980 independent reflections with sinθ/λ ≤ 0.62 Å^{-1}, 1444 had I ≥ 2.5σ(I) and were considered as observed. The structure was solved by direct methods (SHELXS-86) [15] and refined by least squares methods [16] to an R-value of 0.035 for the observed reflections. The atomic coordinates are recorded in Table 2, and the bond lengths and angles are given in Tables 6 and 7. Figure 1 shows a view of the molecule with numbering scheme and selected bond lengths [17].

Table 6

Bond Lengths (Å) with Standard Deviations in Parentheses

Compound **8**			Compound **9**			Compound **10**			Compound **11**		
N2	---S1	1.667(2)	N2	-S1	1.761(3)	N2	---S1	1.672(3)	N2	---S1	1.687(5)
N3	---N2	1.310(3)	O8	-S1	1.963(3)	O8	---S1	2.119(3)	O8	---S1	2.229(4)
C5	---C4	1.386(3)	C9	-N2	1.452(5)	C4	---N3	1.366(3)	C16	---N2	1.471(8)
C6	---C5	1.424(3)	C5	-C4	1.391(5)	C5	---C4	1.375(4)	C5	---C4	1.393(7)
O8	---N7	1.292(2)	C6	-C5	1.421(6)	C6	---C5	1.412(5)	C6	---C5	1.418(8)
C11	---C10	1.388(3)	O8	-N7	1.338(5)	O8	---N7	1.326(4)	O8	---N7	1.304(5)
C12	---C11	1.389(3)	C15	-C10	1.399(6)	C15	---C10	1.392(4)	C11	---C10	1.396(8)
C14	---C13	1.368(4)	C13	-C12	1.377(8)	C13	---C12	1.368(5)	C12	---C11	1.371(8)
C5	---S1	1.697(2)	C15	-C14	1.389(7)	C15	---C14	1.387(5)	C14	---C13	1.365(9)
C4	---N3	1.361(3)	C5	-S1	1.701(4)	C5	---S1	1.712(3)	F18	---B17	1.366(9)
C10	---C4	1.477(3)	N3	-N2	1.310(4)	N3	---N2	1.306(3)	F20	---B17	1.340(9)
N7	---C6	1.302(3)	C4	-N3	1.350(5)	C9	---N3	1.467(4)	C5	---S1	1.695(5)
C9	---N7	1.460 (3)	C10	-C4	1.475(6)	C10	---C4	1.466(4)	N3	---N2	1.322(6)
C15	---C10	1.391(3)	N7	-C6	1.302(6)	N7	---C6	1.309(4)	C4	---N3	1.330(6)
C13	---C12	1.380(4)	C11	-C10	1.383(6)	C11	---C10	1.390(4)	C10	---C4	1.471(7)
C15	---C14	1.384(3)	C12	-C11	1.371(7)	C12	---C11	1.374(5)	N7	---C6	1.307(7)
			C14	-C13	1.354(8)	C14	---C13	1.373(5)	C9	---N7	1.474(9)
									C15	---C10	1.379(8)
									C13	---C12	1.368(10)
									C15	---C14	1.383(8)
									F19	---B17	1.368(10)
									F21	---B17	1.317(9)

Table 7

Bond Angles (°) with Standard Deviations in Parentheses

Compound **8**			
C5	-S1	-N2	92.8(1)
C4	-N3	-N2	113.1(2)
C10	-C4	-N3	120.2(2)
C4	-C5	-S1	107.8(2)
C6	-C5	-C4	127.2(2)
O8	-N7	-C6	122.1(2)
C9	-N7	-O8	116.7(2)
C15	-C10	-C4	120.3(2)
C12	-C11	-C10	120.4(2)
C14	-C13	-C12	120.0(2)
C14	-C15	-C10	119.5(2)
N3	-N2	-S1	112.4(2)
C5	-C4	-N3	113.8(2)
C10	-C4	-C5	126.0(2)
C6	-C5	-S1	124.8(2)
N7	-C6	-C5	120.6(2)
C9	-N7	-C6	121.2(2)
C11	-C10	-C4	120.4(2)
C15	-C10	-C11	119.3(2)
C13	-C12	-C11	119.7(2)
C15	-C14	-C13	121.0(2)

Compound **9**			
C5	-S1	-N2	85.8(2)
O8	-S1	-C5	83.8(2)
C9	-N2	-S1	123.0(3)
C4	-N3	-N2	109.9(3)
C10	-C4	-N3	118.9(3)
C4	-C5	-S1	113.3(3)
C6	-C5	-C4	131.9(4)
O8	-N7	-C6	111.7(4)
C11	-C10	-C4	121.1(4)
C15	-C10	-C11	119.0(4)
C13	-C12	-C11	120.1(5)
C15	-C14	-C13	121.0(5)
O8	-S1	-N2	169.5(2)
N3	-N2	-S1	117.1(3)
C9	-N2	-N3	119.8(3)
C5	-C4	-N3	113.8(3)
C10	-C4	-C5	127.3(3)
C6	-C5	-S1	114.7(3)
N7	-C6	-C5	117.5(4)
N7	-O8	-S1	112.2(2)
C15	-C10	-C4	119.9(4)
C12	-C11	-C10	120.7(5)
C14	-C13	-C12	120.2(5)
C14	-C15	-C10	119.1(5)

Compound **10**			
C5	-S1	-N2	92.0(1)
O8	-S1	-C5	80.0(1)
C4	-N3	-N2	117.7(3)
C9	-N3	-C4	124.5(3)
C10	-C4	-N3	122.2(3)
C4	-C5	-S1	110.6(2)
C6	-C5	-C4	131.1(3)
O8	-N7	-C6	111.9(3)
C11	-C10	-C4	120.9(3)
C15	-C10	-C11	119.6(3)
C13	-C12	C11	120.9(4)
C15	-C14	-C13	120.1(4)
O8	-S1	-N2	171.9(1)
N3	-N2	-S1	110.2(2)
C9	-N3	-N2	117.8(3)
C5	-C4	-N3	109.4(3)
C10	-C4	-C5	128.3(3)
C6	-C5	-S1	118.3(2)
N7	-C6	-C5	118.7(3)
N7	-O8	-S1	111.0(2)
C15	-C10	-C4	119.5(3)
C12	-C11	-C10	119.6(3)
C14	-C13	-C12	120.2(4)
C14	-C15	-C10	119.6(3)

Compound **11**			
C5	-S1	-N2	87.7(3)
C16	-N2	-S1	122.3(4)
C4	-N3	-N2	109.3(4)
C10	-C4	-N3	118.5(5)
C4	-C5	-S1	111.1(4)
C6	-C5	-C4	128.8(5)
O8	-N7	-C6	119.5(5)
C9	-N7	-O8	116.8(5)
C15	-C10	-C4	121.1(5)
N3	-N2	-S1	117.5(4)
C16	-N2	-N3	120.2(5)
C5	-C4	-N3	114.4(5)
C10	-C4	-C5	127.0(5)
C6	-C5	-S1	120.1(4)
N7	-C6	-C5	115.6(5)
C9	-N7	-C6	123.5(5)
C11	-C10	-C4	119.9(5)
C15	-C10	-C11	119.0(6)
C13	-C12	-C11	121.1(7)
C15	-C14	-C13	119.8(7)
F19	-B17	-F18	109.3(7)
F20	-B17	-F19	109.4(8)
F21	-B17	-F19	111.4(8)
C12	-C11	-C10	119.4(6)
C14	-C13	-C12	120.0(7)
C14	-C15	-C10	120.7(6)
F20	-B17	-F18	106.2(7)
F21	-B17	-F18	109.1(8)
F21	-B17	-F20	111.3(8)

Crystal Structure Analysis of **9**.

Compound **9** crystallized from ethanol in the space group Pcab with a = 7.514(2), b = 10.468(2), c = 25.771(6) Å, V = 2027.1(9) Å^3, Z = 8, D_x = 1.44 g cm^{-3}. Intensities from a parallelepiped crystal 0.4 x 0.2 x 0.05 mm were measured using a Huber 4-circle diffractometer with graphite monochromatized MoKα radiation (λ = 0.71069 Å). Of the 1990 independent reflections with $\sin\theta/\lambda \leq 0.62$ Å^{-1}, 1133 had $I \geq 2.5\sigma(I)$ and were considered as observed. The structure was solved by direct methods (SHELXS-86) [15] and refined by least squares methods [16] to an R-value of 0.049 for the observed reflections. The atomic coordinates are recorded in Table 3, and the bond lengths and angles are given in Tables 6 and 7. Figure 2 shows a view of the molecule with numbering scheme and selected bond lengths [17].

Crystal Structure Analysis of **10**.

Compound **10** crystallized from ethanol in the space group P2$_1$/n with a = 11.660(4), b = 7.259(4), c = 13.173(4) Å, β = 116.18(3)°, V = 1000.6(7) Å^3, Z = 4, D_x = 1.46 g cm^{-3}. Intensities from a parallelepiped crystal 0.4 x 0.25 x 0.07 mm were measured using a Huber 4-circle diffractometer with graphite monochromatized MoKα radiation (λ = 0.71069 Å). Of the 1964 independent reflections with $\sin\theta/\lambda \leq 0.62$ Å^{-1}, 1193 had $I \geq 2.5\sigma(I)$ and were considered as observed. The structure was solved by direct methods (SHELXS-86) [15] and refined by least squares methods [16] to an R-value of 0.042 for the observed reflections. The atomic coordinates are recorded in Table 4, and the bond lengths and angles are given in Tables 6 and 7. Figure 3 shows a view of the molecule with numbering scheme and selected bond lengths [17].

Crystal Structure Analysis of **11**.

Compound **11** crystallized from ethanol in the space group P2$_1$/n with a = 11.046(1), b = 7.775(1), c = 16.394(2) Å, β = 91.73(1)°, V = 1407.3(3) Å^3, Z = 4, D_x = 1.52 g cm^{-3}. Intensities from a parallelepiped crystal 0.15 x 0.22 x 0.23 mm were measured using a Huber 4-circle diffractometer with graphite monochromatized MoKα radiation (λ = 0.71069 Å). Of the 2771 independent reflections with $\sin\theta/\lambda \leq 0.62$ Å^{-1}, 1351 had $I \geq 2.5\sigma(I)$ and were considered as observed. The structure was solved by direct methods (SHELXS-86) [15] and refined by least squares methods [16] to an R-value of 0.064 for the observed reflections. The atomic coordinates are recorded in Table 5, and the bond lengths and angles are given in Tables 6 and 7. Figure 4 shows a view of the molecule with numbering scheme and selected bond lengths [17].

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