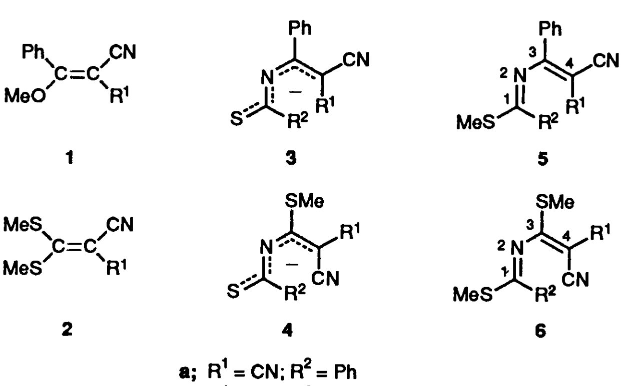
One-pot Stereoselective Synthesis and Structural Study of 1-Methylthio-2-azabuta-1,3-diene-4-carbonitriles

Antonio Lorente,[*,a] **José L. Balcázar**[b] **and Feliciana Florencio**[c]
[a] *Departamento de Química Orgánica, Universidad de Alcalá, 28871, Alcalá de Henares, Madrid, Spain*
[b] *Departamento de Ciencias Analíticas, U.N.E.D., Senda del Rey s/n, 28040, Madrid, Spain*
[c] *U.E.I. de Cristalografía, Instituto Rocasolano, C.S.I.C., Serrano 119, 28006, Madrid, Spain*

The methylation of the carbanion resulting from addition of thioamides to methoxymethylene compounds **1** or ketene dithioacetals **2** affords two series of 1-methylthio-2-azabuta-1,3-diene-4-carbonitriles **5** or **6**. The IR, MS and ^1H and ^{13}C NMR spectral properties are reported. X-Ray crystallographic analyses established the *E* stereochemistry of the C–N double bond in all cases studied. Isomerization of the C–N double bond was achieved by treatment of the 2-aza dienes **5a** and **6a** with sodium methanethiolate in propan-2-ol at room temperature.

[4 + 2] Cycloaddition of 2-azabuta-1,3-dienes to dienophiles is a useful tool for the synthesis of six-membered nitrogen-containing heterocycles with a defined substitution pattern.[1,2] However the lack of general methods for the synthesis of 2-aza-1,3-dienes has limited the utility of this process. More recent methods to obtain this type of product reported in the literature consist of thermal ring opening of heterocyclic compounds[3–6] and Diels–Alder adducts.[7,8] Reaction of imines[9–11] or enamines[12] with electrophiles, *O*-silylation of imides,[13] dehydrochlorination of α-chloroimines,[14] and condensation of ammoniopropanedinitrile with aromatic aldehydes,[15] are other routes to aza-1,3-dienes. This paper presents a one-pot stereoselective synthesis of 2-azabuta-1,3-dienes with electron-donating and electron-withdrawing groups. In previous papers[16–19] we have reported the synthesis of 4-thioxo-3*H*-pyrimidines by reaction of methoxymethylene compounds **1** or ketene dithioacetals **2** with thioamides. The reaction proceeds by a Michael-type addition of the thioamide to the unsaturated compound **1** or **2** followed by cyclization in acid medium. Methylation *in situ* of the carbanion **3** or **4** formed in the first step of the process affords the 2-azabuta-1,3-dienes **5** or **6** with moderate to good yields. In all cases regioselective methylation of the sulfur and *E*-stereoselectivity in the formation of C–N double bond was observed. This stereoselectivity can be explained assuming that the *E*-conformation is the most stable for adducts **3** or **4**.



1 **3** **5**
2 **4** **6**

a; R^1 = CN; R^2 = Ph
b; R^1 = CN; R^2 = Me
c; R^1 = CO_2Me; R^2 = Ph
d; R^1 = CO_2Me; R^2 = Me

Results and Discussion

The adducts **3** and **4** were generated from the corresponding thioamides and unsaturated compounds **1** or **2** using NaH as the base in dimethylformamide (DMF) at room temperature. The solution of the adduct was methylated at the same temperature and the 1-methylthio-2-azabuta-1,3-diene-4-carbonitriles **5** or **6** were identified from spectroscopic and X-ray diffraction data. The compounds **5** and **6** thus obtained are stable and retain their stereochemistry in solution at relatively high temperature (80 °C). Isomerization of the C–N double bond was achieved by treatment of the corresponding 2-aza diene with sodium methanethiolate in propan-2-ol at room temperature. Thus (*E*)-2-aza dienes **5a** and **6a** were transformed into the (*Z*)-isomers **7** and **8** respectively.

7 **8**

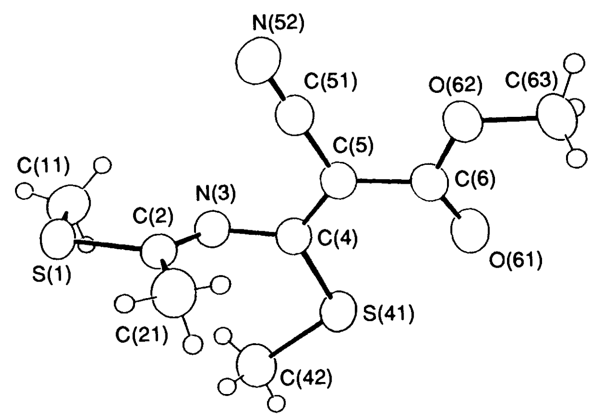
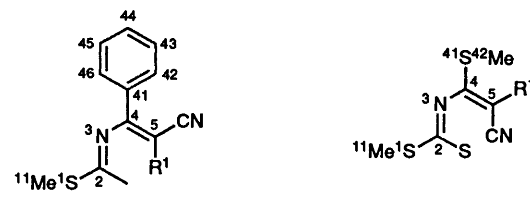


Fig. 1 ORTEP view of compound **6d** showing the crystallographic numbering

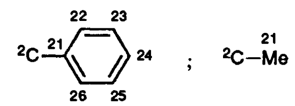
Structural Study.—In previous papers[20] we reported the radiocrystallographic study of compounds **5a**, **5c**, **5d** and **6b**. Now we describe the structure of **6d** and a comparative study of all these structures.

Description of the structure of compound **6d**. Positional parameters are given in Table 4. Fig. 1 displays the structural formula.

Table 1 Selected geometric parameters and crystallographic numbering for compounds **5** and **6**. The two values for **5a** and **6b** are for molecules A, B respectively



5 **6**



	5a	**5c**	**5d**	**6b**	**6d**
Bond lengths (Å)					
C(2)–N(3)	1.275(5), 1.275(4)	1.263(2)	1.273(2)	1.277(3), 1.276(3)	1.272(2)
S(1)–C(2)	1.751(4), 1.741(4)	1.738(2)	1.746(2)	1.749(2), 1.729(2)	1.739(2)
C(4)–S(41)				1.735(2), 1.734(3)	1.734(2)
C(4)–C(5)	1.352(6), 1.370(5)	1.367(3)	1.370(3)	1.377(3), 1.374(3)	1.377(2)
Bond angles (°)					
S(1)–C(2)–C(21)	114.0(3), 114.9(3)	113.6(1)	114.1(2)	114.0(2), 113.7(2)	114.1(1)
N(3)–C(2)–C(21)	125.8(4), 125.1(4)	124.9(2)	125.3(2)	125.7(3), 125.7(2)	125.7(2)
Torsion angles (°)					
C(22)–C(21)–C(2)–N(3)	140.8(4), 125.3(4)	−122.1(2)			
C(2)–N(3)–C(4)–C(5)	68.8(6), 81.3(5)	−80.9(3)	−82.0(3)	80.6(3), −84.1(3)	−86.3(2)
C(11)–S(1)–C(2)–N(3)	9.4(4), 3.7(4)	−7.8(2)	−0.2(3)	4.8(3), −2.9(3)	5.8(2)
C(42)–C(41)–C(4)–C(5)	−139.6(4), −148.1(4)	−43.0(3)	126.5(3)		
C(5)–C(4)–S(41)–C(42)				179.2(2), −170.0(2)	175.1(2)

Structure and stereochemistry of compounds **5** *and* **6**. Table 1 shows selected geometric parameters for compounds **5** and **6**. In the cases considered a great deviation from coplanarity for the azadiene framework was observed and this suggests that conjugation between the C(2)–N(3) and C(4)–C(5) double bonds is precluded. The methylthio group at C(2) is almost coplanar with the C(2)–N(3) double bond and adopts a *syn* conformation that allows delocalization of non-bonded electrons on sulfur into the imino group and $n \longrightarrow \sigma^*$ stabilizing electronic interaction. This conjugation produces a shortening of the S(1)–C(2) bond and a lengthening of the C(2)–N(3) double bond that presents a length near to the calculated by Häfelinger[21] for related compounds. The same effects have been observed in the S(41)–C(4) and C(4)–C(5) bonds for compounds **6b** and **6d**. The S(1)–C(2)–C(21) bond angle is contracted whereas the N(3)–C(2)–C(21) is correspondingly expanded in approximately the same extension. These deviations can be explained as a consequence of steric effects of substituents on C(2) and C(5). The phenyl ring at C(2) is twisted with rapport to the plane of the imino function [C(22)–C(21)–C(2)–N(3) torsion angle] that precludes the conjugation. The stereochemistry of the C(2)–N(3) and C(4)–C(5) double bonds is *E* and *Z* respectively in all cases considered. The *Z*-geometry of the C(4)–C(5) double bond in compound **6d** can be explained taking into account that in this configuration an attractive nonbonded S(41)···O=C interaction is possible. In fact the S···O interatomic distance of 2.76 Å is considerably less than the sum of the S and O van der Waals radii (3.25 Å).[22] Interactions of this type have been reported in the literature.[23]

Spectral Properties.—The IR spectra of compounds **5** show absorptions at 2210 cm^{-1} assigned to the conjugated cyano groups and at *ca.* 1725 cm^{-1} consistent with the presence of conjugated ester groups. The same type of absorptions for compounds **6** appear at *ca.* 2200 and 1690 cm^{-1} respectively. The ^1H and ^{13}C NMR spectra of compounds **5** and **6** are summarized in Tables 2 and 3. The inequivocal assignment of ^1H resonances for the methylthio groups in compounds **6** has been made by comparison with the spectra of the 1-trideuteromethylthio-2-azabuta-1,3-dienes analogues. The ^1H and ^{13}C NMR spectra of compounds **5c**, **d** and **6c**, **d** show splitting of signals that can be related with the presence of conformers (ratio 0.25:1). The chemical shift of the methylthio group on the iminyl carbon is not affected by the geminal substituent showing analogous values to those reported in the literature[24] for related compounds. This fact together with the chemical shifts for the aromatic hydrogens in **5a**, **c** and **6a**, **c** indicate that the phenyl ring is twisted out in solution as it is in the solid state for **5a**, **c**. The protons of methylthio at C-1 for compounds (*Z*)-**7** and -**8** are deshielded ($\Delta\delta$ ~0.20) in relation to the same hydrogens of (*E*)-isomers. This fact together with the chemical shifts for the *ortho* aromatic protons (δ ~8.30–8.66) indicate that the phenyl ring in compounds (*Z*)-**7** and -**8** is coplanar with the C–N double bond and exerts an anisotropic deshielding influence on the methylthio group. This fact is consistent with an *anti*-conformation for the SMe in these compounds. The ^{13}C NMR spectra show resonances at *ca.* 162 ppm assignable to a conjugated ester group. The signals at lower field at 171–176 and 182 ppm are assigned to the imino group of compounds **5** and **6** respectively. The resonance of this group undergoes an upfield shift by replacement of phenyl by a methyl group. On the other hand the C-4 of the azadienes **5c**, **d** and **6c**, **d** are deshielded ($\Delta\delta$ ~20) in relation to the same carbon of azadienes **5a**, **b** and **6a**, **b** in accordance with the lower deshielding effect on this carbon exerted by the methoxy-

Table 2 ^1H NMR Chemical shifts for compounds **5** and **6** at 80 MHz

	δ_H							
	5a	**5b**	**5c**	**5d**	**6a**	**6b**	**6c**	**6d**
CH_3		2.26		2.07, 2.19		2.35		2.14, 2.19
CH_3S–C(1)	2.57	2.50	2.48	2.41, 2.43	2.53	2.49	2.53, 3.38	2.42, 2.45
CH_3S–C(2)					2.58	2.40	2.37	2.25, 2.27
CO_2CH_3			3.50, 3.64	3.61, 3.72			3.58, 3.64	3.62, 3.71
Aromatics	7.39–7.65 (m)	7.57–7.75 (m)	7.09–7.68 (m)	7.41–7.80 (m)	7.55 (s)		7.56 (m)	

Table 3 ^{13}C NMR Chemical shifts for compounds **5** and **6** at 75 MHz

	δ_C							
	5a	**5b**	**5c**	**5d**	**6a**	**6b**	**6c**	**6d**
CH_3–S	15.56	14.36	15.04, 15.06 15.08	13.98	14.48, 15.70	13.95, 14.31	13.85, 14.72 15.35, 15.51	13.28, 13.30 14.06, 14.20
CH_3		23.88		23.43, 23.68		23.31		22.85, 23.15
CH_3–O			52.26, 52.31 52.35	52.30			51.93, 52.06	51.78, 51.89, 51.92, 51.96
C-4	51.36	65.48	83.71	84.92	58.63	60.21	80.69	81.32, 81.36
CN	113.80, 114.51	113.58, 114.35	117.64	117.51	113.11, 113.38	112.72, 113.09	115.86	115.39, 116.20
C=O			162.25, 162.59	162.25			163.73	161.11, 163.58
C-3	174.48 [a]	173.41 [b]	167.84, 170.76	167.21, 169.45	175.88	175.99	172.30	171.51, 172.65
C=N	176.61 [a]	177.06 [b]	171.71, 174.21	173.09, 174.92	183.35	184.0	181.9	182.42

[a,b] These values may be interchanged.

carbonyl in comparison with the shielding effect of the cyano group. The mass spectra of compounds **5** and **6** show, in all cases, the ions corresponding to the loss of SMe and R^2(Me)-C=N radicals. This last fragmentation corresponds in most cases to the parent peak of the spectra.

Experimental

Melting points were determined with a Büchi SMP-20 are are uncorrected. IR spectra were recorded on a Perkin-Elmer 883 spectrophotometer. NMR spectra were performed on a Varian FT-80 A (for ^1H) and Varian Unity 300 (for ^{13}C) in $(CD_3)_2SO$ solution. Mass spectra were obtained with a Hewlett Packard HP-5988 at 70 eV. Microanalyses were performed in a Perkin-Elmer 240. Flash column chromatography was carried out on silica gel SDS (230–400 mesh). Methoxymethylene compounds **1** were prepared as previously reported procedures.[25,26] Ketene dithioacetals **2** were prepared according to the procedure described by Gompper and Töpfl.[27]

General Procedure for the Preparation of 2-*Aza*-1,3-*dienes* **5**.—To a suspension of 80% NaH (90 mg, 3 mmol) in dry DMF (30 cm^3) the corresponding thioamide (2 mmol) and methoxymethylene compound **1** (2 mmol) were added. The mixture was stirred at room temperature for 48 h and then methyl iodide (187 mm^3, 3 mmol) was added. After 12 h at room temperature the solution was poured into water (500 cm^3) and the precipitate formed was collected and recrystallized from propan-2-ol.

(E)-1-*Methylthio*-1,3-*diphenyl*-2-*azabuta*-1,3-*diene*-4,4-*dicarbonitrile* **5a**. As yellow crystals (510 mg, 84%); m.p. 115–116 °C; ν_{max}(KBr)/cm^{-1} 2210, 1600, 1505 and 1480; *m/z* 303 (M^+, 33%), 256 (100), 153 (93), 126 (17) and 77 (24) (Found: C, 71.1; H, 4.35; N, 14.0. $C_{18}H_{13}N_3S$ requires C, 71.26; H, 4.32; N, 13.85%).

(E)-1-*Methyl*-1-*methylthio*-3-*phenyl*-2-*azabuta*-1,3-*diene*-4,4-*dicarbonitrile* **5b**. Work-up of reaction mixture yields an oil after pouring into water. The crude product obtained after extraction with diethyl ether was purified by flash column chromatography using hexane–ethyl acetate (12:1) as eluent; 285 mg, 59% as white crystals; m.p. 86–87 °C; ν_{max}(KBr)/cm^{-1} 2210, 1615, 1520 and 1480; *m/z* 241 (M^+, 39%), 194 (72), 153 (100), 126 (12) and 77 (16) (Found: C, 64.9; H, 4.55; N, 13.5. $C_{13}H_{11}N_3S$ requires C, 64.71; H, 4.59; N, 13.29%).

(1E,3Z)-*Methyl* 4-*cyano*-1-*methylthio*-1,3-*diphenyl*-2-*azabuta*-1,3-*diene*-4-*carboxylate* **5c**. As white crystals (639 mg, 95%); m.p. 155–156 °C; ν_{max}(KBr)/cm^{-1} 2211, 1723, 1637, 1595, 1515, 1483 and 1440; *m/z* 336 (M^+, 7%), 305 (6), 290 (21), 289 (100), 277 (9), 186 (49), 143 (9), 142 (78), 127 (37), 121 (10), 115 (15), 105 (8), 100 (11) and 77 (23) (Found: C, 67.6; H, 4.6; N, 8.6. $C_{19}H_{16}N_2O_2S$ requires C, 67.84; H, 4.79; N, 8.33%).

(1E,3Z)-*Methyl* 4-*cyano*-1-*methyl*-1-*methylthio*-3-*phenyl*-2-*azabuta*-1,3-*diene*-4-*carboxylate* **5d**. As white crystals (461 mg, 84%); m.p. 107–108 °C; ν_{max}(KBr)/cm^{-1} 2212, 1727, 1642, 1576, 1531, 1484 and 1430; *m/z* 274 (M^+, 5%), 228 (11), 227 (77), 202 (13), 186 (74), 171 (14), 143 (11), 142 (100), 127 (46), 115 (22), 104 (12), 100 (23), 77 (19), 76 (14), 75 (28) and 59 (80) (Found: C, 61.35; H, 5.05; N, 10.1. $C_{14}H_{14}N_2O_2S$ requires C, 61.29; H, 5.14; N, 10.21%).

(Z)-1-*Methylthio*-1,3-*diphenyl*-2-*azabuta*-1,3-*diene*-4,4-*dicarbonitrile* **7**.—To a solution of **5a** (303 mg, 1 mmol) in propan-2-ol (40 cm^3) sodium methanethiolate (140 mg, 2 mmol) was added. The resulting mixture was stirred at room temperature for 24 h and the precipitate formed was filtered, washed with water and recrystallized from ethanol; 87% yield, m.p. 169–170 °C; ν_{max}(KBr)/cm^{-1} 2216, 1514, 1489, 1443 and 1380; δ_H 2.78 (s, 3 H, SCH_3), 7.59 (s, 6 H, ArH), 7.83–8.17 (m, 2 H, ArH) and 8.30–8.66 (m, 2 H, ArH); *m/z* 303 (M^+, 42%), 302 (100), 256 (3), 224 (4), 200 (6), 153 (21), 127 (38), 104 (26), 103 (12), 97 (9) and 77 (35) (Found: C, 71.05; H, 4.25; N, 14.05. $C_{18}H_{13}N_3S$ requires C, 71.26; H, 4.32; N, 13.85%).

General Procedure for Synthesis of 2-*Azabuta*-1,3-*dienes* **6**.—To a suspension of 80% NaH (225 mg, 7.5 mmol) in anhydrous DMF (20 cm^3) the corresponding thioamide (5 mmol) and ketene dithioacetal **2** (5 mmol) were added. The reaction mixture was stirred at room temperature for 72 h and then dimethylsulfate (755 mm^3, 8 mmol) was added. After 12 h

Table 4 Non-hydrogen atom coordinates for compound **6d** with esds in parentheses

Atom	*x*	*y*	*z*
S(1)	0.255 45(6)	0.019 76(3)	0.623 59(7)
C(11)	0.244 41(34)	−0.028 07(22)	0.373 09(34)
C(2)	0.288 73(19)	−0.112 53(13)	0.695 06(22)
C(21)	0.280 46(33)	−0.101 93(19)	0.894 13(28)
N(3)	0.314 04(18)	−0.207 33(11)	0.580 30(19)
C(4)	0.342 10(21)	−0.314 90(13)	0.628 85(21)
S(41)	0.147 96(6)	−0.404 81(4)	0.523 03(6)
C(42)	−0.045 94(27)	−0.308 25(19)	0.415 24(35)
C(5)	0.521 02(21)	−0.351 87(13)	0.741 52(23)
C(51)	0.674 20(24)	−0.273 77(15)	0.814 34(27)
N(52)	0.795 58(26)	−0.210 47(16)	0.872 08(34)
C(6)	0.560 44(22)	−0.468 72(13)	0.783 83(23)
O(61)	0.444 52(19)	−0.543 29(11)	0.718 85(23)
O(62)	0.741 70(17)	−0.482 48(11)	0.905 29(19)
C(63)	0.793 45(32)	−0.596 72(19)	0.951 43(35)

at room temperature the solution was concentrated up to dryness and the oily residue thus obtained was taken in dichloromethane, washed with water and dried ($MgSO_4$). Solvent was removed under reduced pressure to afford crude product which was purified by crystallization.

The 1-trideuteromethylthio-2-azabuta-1,3-dienes ([$^2H_3$]-**6**) were prepared by the same procedure using [$^2H_3$]-methyl iodide as methylating agent.

(E)-1,3-*Dimethylthio*-1-*phenyl*-2-*azabuta*-1,3-*diene*-4,4-*dicarbonitrile* **6a**. As yellow crystals (861 mg, 63%); m.p. 123–124 °C (from propan-2-ol); ν_{max}(KBr)/cm^{-1} 2216, 2206, 1590, 1575, 1455 and 1440; *m/z* 273 (M^+, 17%), 226 (50), 153 (14), 123 (100), 121 (19), 108 (13), 103 (9), 96 (13), 82 (5), 79 (21) and 77 (29) (Found: C, 57.2; H, 4.1; N, 15.05. $C_{13}H_{11}N_3S_2$ requires C, 57.12; H, 4.06; N, 15.37%).

(E)-1-*Methyl*-1,3-*dimethylthio*-2-*azabuta*-1,3-*diene*-4,4-*dicarbonitrile* **6b**. As yellow crystals (665 mg, 63%); m.p. 81–82 °C (from ethanol); ν_{max}(KBr)/cm^{-1} 2200, 1605, 1460 and 1420; *m/z* 211 (M^+, 20%), 164 (41), 123 (100), 108 (15), 96 (9) and 79 (13) (Found: C, 45.2; H, 4.4; N, 19.7. $C_8H_9N_3S_2$ requires C, 45.47; H, 4.29; N, 19.89%).

(1E,3Z)-*Methyl* 4-*cyano*-1,3-*dimethylthio*-1-*phenyl*-2-*azabuta*-1,3-*diene*-4-*carboxylate* **6c**. As yellow crystals (1.03 g, 67%); m.p. 176–177 °C (from propan-2-ol); ν_{max}(KBr)/cm^{-1} 2190, 1680, 1590, 1450 and 1436; *m/z* 306 (M^+, 7%), 291 (2), 275 (10), 259 (80), 247 (48), 156 (100), 121 (22), 112 (39), 97 (33) and 77 (32) (Found: C, 54.7; H, 4.8; N, 9.05. $C_{14}H_{14}N_2O_2S_2$ requires C, 54.88; H, 4.61; N, 9.14%).

(1E,3Z)-*Methyl* 4-*cyano*-1-*methyl*-1,3-*dimethylthio*-2-*azabuta*-1,3-*diene*-4-*carboxylate* **6d**. As yellow crystals (928 mg, 76%); m.p. 92–93 °C (from ethanol); ν_{max}(KBr)/cm^{-1} 2190, 1695, 1605, 1460 and 1415; *m/z* 244 (M^+, 7%), 213 (5), 198 (6), 197 (70), 157 (5), 156 (68), 112 (35), 98 (6), 97 (45), 91 (16), 82 (13), 75 (32), 73 (7), 71 (19), 70 (11) and 59 (100) (Found: C, 44.1; H, 4.8; N, 11.7. $C_9H_{12}N_2O_2S_2$ requires C, 44.24; H, 4.95; N, 11.47%).

Crystal data. $C_9H_{12}N_2O_2S_2$, $M = 224.3$. Triclinic, $a = 7.777(2)$, $b = 11.819(2)$, $c = 7.535(2)$ Å, $\alpha = 105.27(1)$, $\beta = 114.77(2)$, $\gamma = 82.56(2)°$, $V = 606.5(3)$ Å^3 (by least-squares refinement from 25 reflections, $\lambda = 0.7107$ Å); space group $P\bar{1}$, $Z = 2$, $D_x = 1.388$ mg m^{-3}. Crystal dimensions: 0.4 × 0.6 × 0.5 mm; μ(Mo-Kα) 4.043 cm^{-1}.

Data collection and processing. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo-Kα radiation; 3571 reflections measured [$2 < \theta < 60°$, $h(0, 10)$, $k(16, -16)$, $l(9, -10)$], 3112 observed with $I > 2\sigma(I)$. Two check reflections measured every 90 min showed no significant variation.

Structure analysis and refinement. Direct methods with MULTAN 80[28] refined by full-matrix least squares analysis, unit weights, with anisotropic temperature factors. All H-atoms located in difference Fourier synthesis, positional parameters included in further refinement with fixed isotropic temperature factors. Final $F = 0.13$ e Å^{-3}, $R = 0.040$ and $R_w = 0.055$. Atomic scattering factors from International Tables for X-ray Crystallography.[29] Calculations performed with XRAY 70,[30] PARST[31] and PESOS[32] on a VAX 11/750 computer. Non-hydrogen atomic coordinates are given in Table 4. Full lists of bond lengths, bond angles, thermal parameters, torsion angles and least squares planes have been deposited at the CCDC.*

(Z)-1,3-*Dimethylthio*-1-*phenyl*-2-*azabuta*-1,3-*diene*-4,4-*dicarbonitrile* **8**.—To a solution of **6a** (273 mg, 1 mmol) in propan-2-ol (40 cm^3) sodium methanethiolate (140 mg, 2 mmol) was added. The reaction mixture was stirred at room temperature for 48 h and then the precipitate formed was filtered, washed with water and recrystallized from propan-2-ol; 52% yield, m.p. 223–224 °C; ν_{max}(KBr)/cm^{-1} 2210, 1507, 1488 and 1440; δ_H 2.76 (s, 6 H, SCH_3), 7.46–7.72 (m, 3 H, ArH) and 8.37–8.62 (m, 2 H, ArH); *m/z* 273 (M^+, 20%), 258 (3), 240 (24), 226 (3), 194 (5), 155 (9), 153 (6), 137 (25), 123 (30), 109 (52), 108 (35), 104 (100), 103 (48), 97 (27), 96 (33), 82 (31), 79 (28) and 77 (60) (Found: C, 57.2; H, 4.1; N, 15.1. $C_{13}H_{11}N_3S_2$ requires C, 57.11; H, 4.06; N, 15.37%).

Acknowledgements

This work was supported by the DGICYT (Spain) Grant PB-88/015.

* For full details of the Cambridge Crystallographic Data Centre deposition scheme see, 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1992, Issue 1.

References

1 D. L. Boger and S. M. Weinreb, *Hetero Diels–Alder Methodology in Organic Synthesis*, Academic Press, New York, 1987, pp. 255–260.
2 F. Fringuelli and A. Taticchi, *Dienes in the Diels–Alder Reaction*, Wiley, New York, 1990.
3 J. Charrier, A. Foucaud, H. Person and E. Loukakov, *J. Org. Chem.*, 1983, **48**, 481.
4 J. C. Guillemin, J. M. Denis and A. Lablache-Combier, *J. Am. Chem. Soc.*, 1981, **103**, 468.
5 L. Ghosez, F. Sainte, M. Rivera, C. Bernard-Henriet and V. Gouverneur, *Recl. Trav. Chim. Pays-Bas*, 1986, **105**, 456.
6 P. Wipf and H. Heimgartner, *Chimia*, 1984, **38**, 357.
7 J. Ripoll, H. Lebrun and A. Thuiller, *Tetrahedron*, 1980, **36**, 2497.
8 Y.-M. Malecot, J.-L. Ripoll and A. Thuiller, *J. Chem. Res. (S)*, 1983, 86.
9 J. Barluenga, J. Joglar, S. Fustero, V. Gotor, C. Krüger and M. J. Romão, *Chem. Ber.*, 1985, **118**, 3652.
10 D. Armesto, M. J. Ortiz and R. Pérez-Ossorio, *J. Chem. Soc., Perkin Trans. 1*, 1986, 2021.
11 D. Armesto, W. M. Horspool, M. J. Ortiz and S. Romano, *J. Chem. Soc., Perkin Trans. 1*, 1992, 171.
12 R. J. P. Corriu, V. Huynh, J. J. E. Moreau and M. Pataud-Sat, *Tetrahedron Lett.*, 1982, **23**, 3257.
13 F. Sainte, B. Serckx-Poncin, A.-M. Hesbain-Frisque and L. Ghosez, *J. Am. Chem. Soc.*, 1982, **104**, 1428.
14 N. De Kimpe, Z.-P. Yao, M. Boeykens and M. Nagy, *Tetrahedron Lett.*, 1990, **31**, 2771.
15 F. Freeman and D. S. H. L. Kim, *Synthesis*, 1989, 698.
16 J. L. Soto, A. Lorente and J. L. García Navío, *An. Quim.*, 1981, **77C**, 255.
17 A. Lorente, J. L. García Navío and J. L. Soto, *J. Heterocycl. Chem.*, 1985, **22**, 49.
18 A. Lorente, J. L. García Navío, L. Fuentes and J. L. Soto, *Synthesis*, 1985, 86.
19 A. Lorente, M. L. García, M. Fernández and J. L. Soto, *Heterocycles*, 1992, **34**, 1573.

20 J. L. Balcázar, F. Florencio and S. García-Blanco, *Acta Crystallogr., Sect. C*, (*a*) 1985, **41**, 1795; (*b*) 1987, **43**, 1438; (*c*) 1988, **44**, 1500; (*d*) 1987, **43**, 1432.
21 G. Häfelinger, *Tetrahedron*, 1971, **27**, 1635.
22 L. Pauling, *The Nature of the Chemical Bond*, Cornell University, Ithaca, New York, 1960, pp. 260–262.
23 N. U. Kamath and K. Venkatesan, *Acta Crystallogr., Sect. C*, 1984, **40**, 1610.
24 W. Walter and C. O. Meese, *Chem. Ber.*, 1977, **110**, 2463.
25 A. Dornow and E. Schleese, *Chem. Ber.*, 1958, **91**, 1830.
26 T. Hayashi, *J. Org. Chem.*, 1966, **31**, 3253.
27 R. Gompper and W. Töpfl, *Chem. Ber.*, 1962, **95**, 2861.
28 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffration Data, University of York, England, 1980.
29 *International Tables for X-ray Crystallography*, vol. IV, Kynoch Press, Birmingham, England, 1974.
30 J. M. Stewart, F. A. Kundell and J. C. Baldwin: *The X-ray 70 System*, Computer Science Center, University of Maryland, College Park, Maryland, USA, 1970.
31 M. A. Nardelli, *Comput. Chem.*, 1983, **7**, 95.
32 M. Martínez-Ripoll and F. H. Cano, *Pesos program*, Instituto Rocasolano, CSIC, Serrano 119, Madrid 28006, Spain, 1975.

Paper 2/03467K
Received 4*th September* 1992
Accepted 7*th September* 1992