THE DIVERSE REACTIVITY OF (BENZOTHIAZOL-2-YLTHIO)-(BENZOTRIAZOL-1-YL)METHANE

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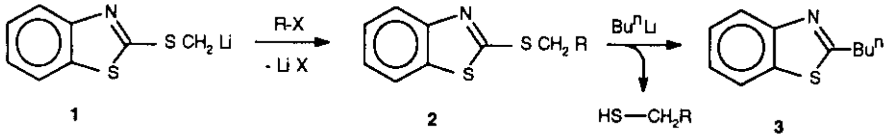
Abstract-The reaction of lithiated (benzothiazol-2-ylthio)(benzotriazol-1-yl)-methane with *n*-propyl iodide yielded: (benzothiazol-2-yl)(benzothiazol-2-ylthio)(benzotriazol-1-yl)methane, (benzothiazol-2-yl)(benzotriazol-1-yl)(propylthio)methane and (benzotriazol-1-yl)(propylthio)methane. Reactions of 2-methylthiobenzothiazole with 1-methylbenzotriazole 2-methylbenzotriazole and (benzotriazol-1-yl)(phenylthio)methane are also described.

INTRODUCTION

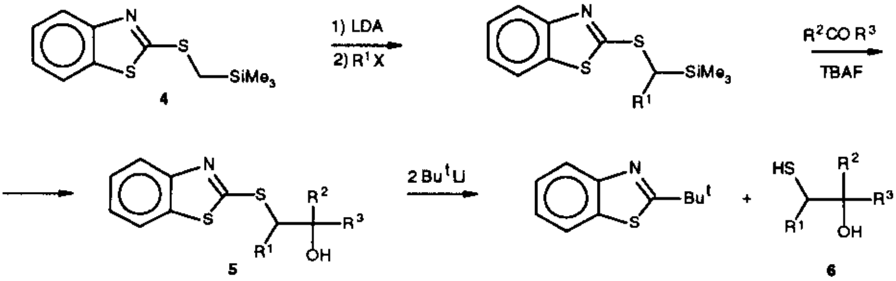
Alkyl halides can be mercaptomethylated by treatment with the lithium salt of 2-methylthiobenzothiazole (**1**).[1] This process involves the displacement of the thioalkyl residue from the alkylated thiobenzothiazole intermediate (**2**) by *n*-butyllithium to afford **3** together with the product RCH_2SH (Scheme 1).

Scheme 1



The range of applicability of this method has been expanded by the use of trimethylsilylated intermediate (**4**).[2] Compounds such as **4** are sufficiently acidic to permit sequential deprotonation, alkylation and treatment with carbonyl containing materials to provide a route to the carbinols (**5**). The latter can be treated with *t*-butyllithium to afford the thioalkylated alcohols (**6**) (Scheme 2).

Scheme 2



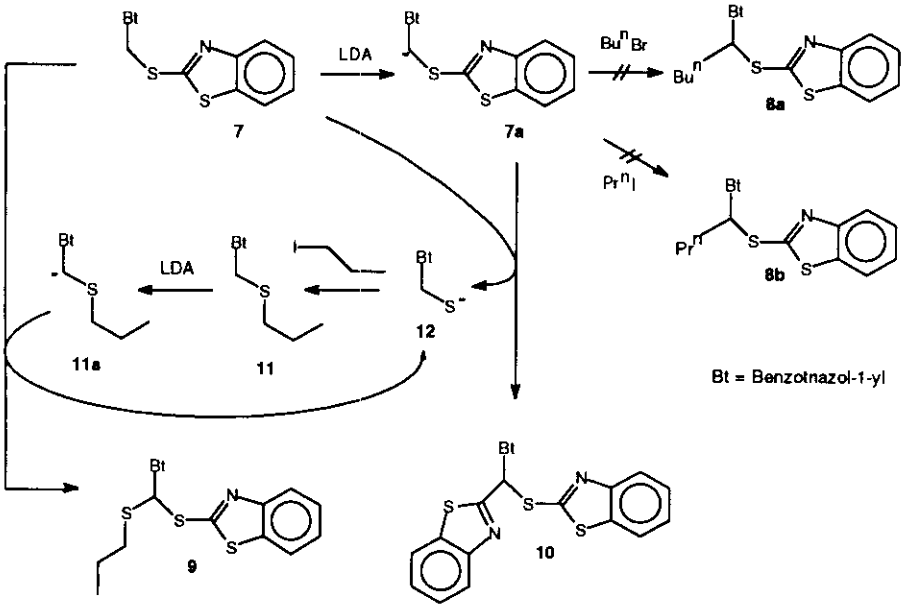
The presence of a benzotriazolyl group permits facile α-lithiation.[3-6] Thus it was expected that (benzothiazol-2-ylthio)(benzotriazol-1-yl)methane (**7**) (Scheme 3) would be a useful extension to the mercaptomethylation methods *vide supra,* since the expected products (**8**) of alkylation should undergo further transformation by displacement of the benzotriazole residue.[7]

RESULTS AND DISCUSSION

(Benzothiazol-2-ylthio)(benzotriazol-1-yl)methane (**7**) was prepared in near quantitative yields by reacting the sodium salt of 2-mercaptobenzothiazole with 1-chloromethylbenzotriazole. However, treating **7** at −78°C with LDA followed by rapid quenching with *n*-butyl bromide did not give the expected **8a**. Likewise, when *n*-propyl iodide was employed, we could not isolate compound (**8b**). Instead, the products (**9**, **10** and **11**) were isolated, each in approximately 25% yield (Scheme 3). The structures of these products were elucidated by nmr, using ^1H-^1H correlations and both direct and long-range ^1H-^{13}C correlations. The structures of **9** and **10** were confirmed by χ-ray crystallography.

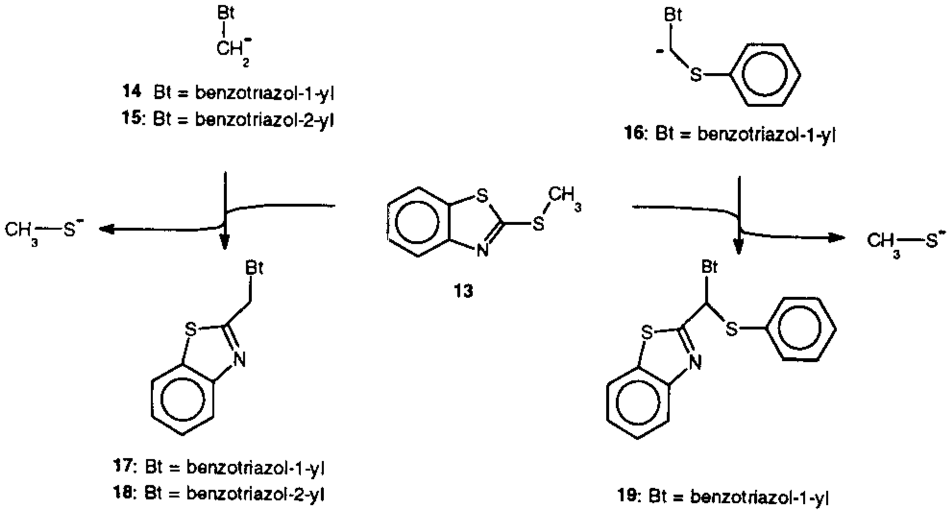
The origins of **9**, **10** and **11** have been rationalized in Scheme 3. Evidently, anion (**7a**) reacts preferentially with more **7** rather than undergoing *C*-alkylation by the alkyl halide. The liberated thiolate (**12**) displaces iodide ion from *n*-propyl iodide to afford **11**. Subsequent deprotonation of **11** gives **11a** which reacts with **7** to regenerate **12**, together with product (**9**).

Scheme 3



We examined the nucleophilic behavior of other benzotriazole stabilized carbanions towards displacement reactions at the C-2 position of 2-alkylthiobenzothiazoles. 2-Methylthiobenzothiazole (**13**) was reacted with the carbanions of 1-methylbenzotriazole (**14**), 2-methylbenzotriazole (**15**) and (benzotriazol-1-yl)(phenylthio)-

Scheme 4



methane (**16**)[8] to give the expected products (benzothiazol-2-yl)(benzotriazol-1-yl)methane (**17**), (benzothiazol-2-yl)-(benzotriazol-2-yl)methane (**18**) and (benzothiazol-2-yl)(benzotriazol-1-yl)(phenylthio)-methane (**19**) in 85%, 55% and 92% yields respectively (Scheme 4).

χ-Ray and Nuclear Magnetic Resonance Determinations

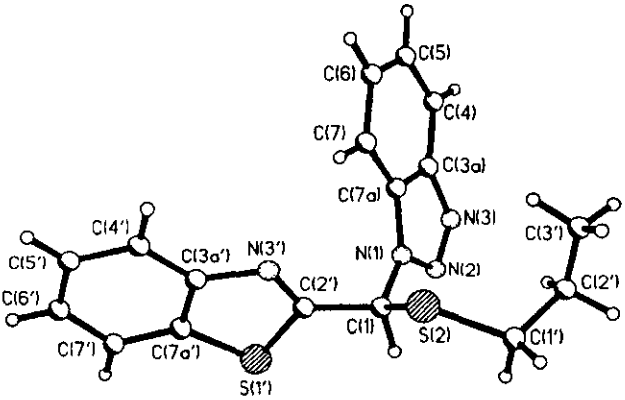


Figure 1. Perspective view and atom labelling of the X-ray structure of 9

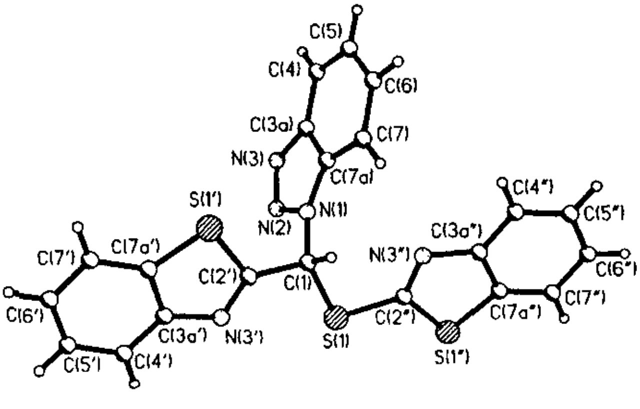


Figure 2. Perspective view and atom labelling of the X-ray structure of 10.

Figure 1 shows a perspective view and atom labelling of the crystal structure of **9**. The two benzazole ring systems are each planar to within 0.011 Å and their mean planes are mutually inclined at an angle of 65.6°. For packing reasons the propyl sidechain is not in the extended conformation but has the methyl group gauche to S(2) [S(2) - C(1') - C(2') - C(3') = 46.3°]. However the high displacement parameters for the methyl carbon do suggest some minor disorder in the orientation of the propyl side chain. Figure 2 shows a perspective view and atom labelling of the crystal structure of **10**. The two benzothiazole rings are approximately coplanar [angle between meanplanes = 8.0°] and approximately orthogonal to the plane of the benzothiazole [76.4°]. This conformation maximizes π-π interactions in the molecular packing.

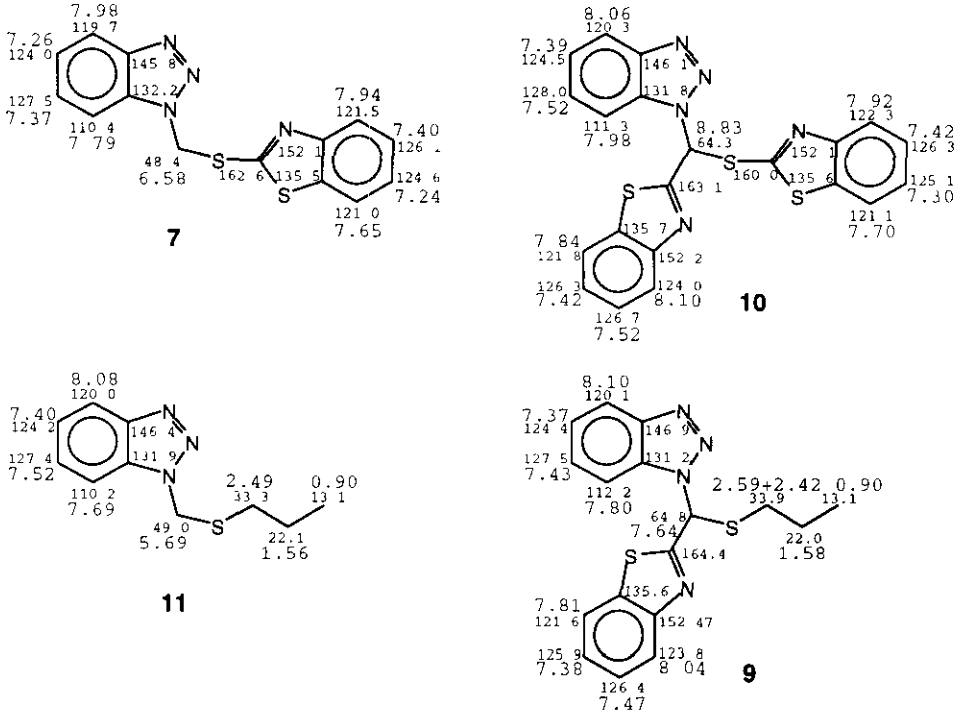
Table 1. Partial ^1H-^1H Coupling Constants.

Compound	δ(ppm)	Mult.*	J(Hz)
9	7.64	s	-----
	2.59	ddd	12.7, 7.8, 6.4
	2.42	ddd	12.7, 7.4, 7.3
	1.58	m	unresolved
	0.90	t	7.3
11	5.69	s	-----
	2.49	t	7.3
	1.56	sx	7.3
	0.90	t	7.3

* s=singlet, d=doublet; t=triplet, sx=sextet; m=multiplet

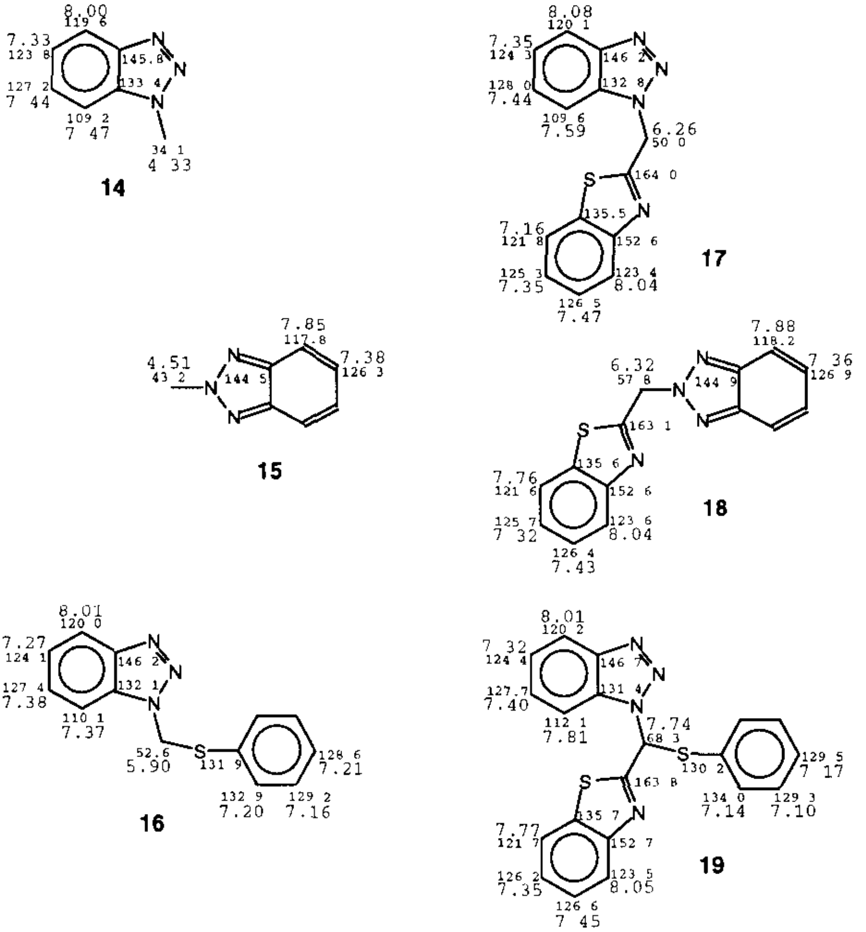
The complete assignments of ^1H and ^{13}C chemical shifts for **7** and **9-11** are presented in Scheme 5. The nmr data corroborated the χ-ray determination for compound (**9**) and discounted structure (**8b**) on the basis of: i) the absence of proton-proton coupling between the proton resonating at 7.64 ppm and those resonating at 2.59 ppm and 2.42 ppm (Table 1), ii) the absence of long-range heteronuclear coupling between the proton resonating at 7.67 ppm and the carbon resonating at 22.0 ppm, together with the fact that the proton at 7.67 ppm is coupled with only 3 carbons (131.2, 164.4 and 33.9 ppm), and iii) the consistency of chemical shifts both for the proton and the carbon resonances of the *n*-propyl chains in compounds (**9**) as compared with **11**.

Scheme 5



The complete assignments of ^1H and ^{13}C chemical shifts for **14-19** are presented in Scheme 6. The observed deshieldings (15.7-15.9 ppm) of the methinyl carbons in compound pairs **7/10**, **11/9**, **14/17**, **15/18** and **16/19** were consistent with the simultaneous presence of the benzothiazol-2-yl and benzotriazol-1-yl moieties.

Scheme 6



CONCLUSION

The present work illustrates the utility of benzotriazolyl substituted molecules (**7**, **14-16**) which also contain other displaceable functional groups. As is demonstrated here, the preparation of the carbanions of these species in the presence of electrophiles, leads to substitution products (**9**, **10**, **17-19**) which are otherwise difficult to obtain. Additionally, these highly functionalized compounds are well suited for further elaboration.

EXPERIMENTAL

Melting points were determined on a Kofler hot-stage microscope and are uncorrected. Nmr spectra were recorded on a Varian VXR-300 spectrometer, using $CDCl_3$ as solvent and TMS as an internal reference. The spectral data is presented in Schemes 5 and 6 and in Table 1. Mass spectra were recorded at 70 eV on a Krafts AEI MS 30 spectrometer. Elemental analyses were performed on a Carlo Erba 1106 elemental analyser.

Tetrahydrofuran (THF) was dried by distillation over the sodium ketyl of benzophenone. All the reactions were carried out under a dry nitrogen atmosphere. Flash column chromatography was carried out on silica gel (EM Merck 60, 230-400 mesh).

(Benzotriazol-1-yl)(benzothiazol-2-ylthio)methane (7). 2-Mercaptobenzothiazole (8.35 g, 50 mmol) was added to a solution of sodium ethoxide prepared from sodium metal (1.15 g, 50 mmol) and absolute ethanol (100 ml) and the mixture stirred for 30 min. 1-Chloromethylbenzotriazole (8.37 g, 50 mmol) was added and the reaction mixture left overnight. The solvent was removed *in vacuo* and the residue dissolved in methylene chloride (150 ml), washed with water (2×50 ml) and dried over $MgSO_4$. Removal of the solvent under reduced pressure yielded a solid which was recrystallized from ethyl acetate to yield (13.71 g, 92%) colorless crystals, mp 109-111°C. *Anal.* Calcd for $C_{14}H_{10}N_4S_2$: C, 56.36; H, 3.38; N, 18.78. Found: C, 56.37; H, 3.35; N, 18.75.

General Procedure for the Reaction of 7 with Alkylhalides.

A THF solution of LDA-mono·THF complex (2.5 ml, 50 mmol) was added by syringe to a solution of **7** (1.49 g, 50 mmol) in THF (40 ml) at -78°C and stirred for 15 min. The alkyl halide (5 mmol) was then added and the mixture stirred at that temperature for a further 5 h. The mixture was permitted to warm to room temperature over 12 h and was quenched by the addition of saturated NH_4Cl (15 ml). The organic layer was separated, dried over $MgSO_4$ and concentrated *in vacuo*. The residue oil was loaded onto a column of flash silica gel and the appropriate fractions collected and purified further as described.

(Benzothiazol-2-yl)(benzothiazol-2-ylthio)(benzotriazol-1-yl)methane (10) was prepared from the reaction of **7** with *n*-butyl bromide as described above. Trituration of the oil separated by column chromatography with ethyl acetate afforded crystals (0.19 g, 18%) mp 148°C. *m/z*: Calcd for $C_{21}H_{14}N_5S_3$: 432.041. Found: 432.039.

(Benzotriazol-1-yl)(thiopropyl)methane (11) was purified by microdistillation (bp 175°C / 1 mm Hg) of the mixture of **11** and (benzothiazol-2-yl)(benzotriazol-1-yl)(propylthio)methane (**9**), eluted from the column as described above to yield (0.25 g, 1.21 mmol) as a colorless oil. *Anal.* Calcd for $C_{10}H_{13}N_3S$: C, 57.95; H, 6.33; N, 20.29. Found: C, 57.95; H, 6.39; N, 20.21.

(Benzothiazol-2-yl)(benzotriazol-1-yl)(propylthio)methane (9) was obtained by the trituration of the residual oil from the distillation described above to give (0.38 g, 1.15 mmol) of colorless crystals mp 94-95°C. *Anal.* Calcd for $C_{16}H_{16}N_4S_2$: C, 59.99; H, 4.74; N, 16.47. Found: C, 59.89; H, 4.72; N, 16.46.

General Procedure for the Reaction of 13 with 14, 15 or 16.

A THF solution of LDA-mono THF complex (20 ml, 40 mmol) was added by syringe to a solution of **13** (4.82 g, 20 mmol) and either **14**, **15** or **16** (20 mmol) in THF (40 ml) at -78°C and stirred at that temperature for 24 h The mixture was quenched by the addition of saturated NH_4Cl (20 ml). The organic layer was separated and the aqueous fraction re-extracted with methylene chloride (3×20 ml). The organic layers were combined, dried over $MgSO_4$ and the solvent was removed *in vacuo* and the product purified as indicated.

(Benzothiazole-2-yl)(benzotriazole-1-yl)methane (17) was obtained by the reaction of **13** with **14**. The residue was triturated first with diethyl ether (1×20 ml) then with ethyl acetate (1×20 ml) to yield **17** (4.52 g, 85%), as colorless crystals, mp 117-118°C. *Anal.* Calcd for $C_{14}H_{10}N_4S$: C, 63.14; H, 3.78; N, 21.04. Found: C, 63.23; H, 3.91; N, 21.05.

(Benzothiazole-2-yl)(benzotriazole-2-yl)methane (18) was obtained by the reaction of **13** with **15**. The residue was chromatographed on silica eluting with hexane and increasing amounts of ether, then recrystallized from ether to yield **18** (2.93 g, 55%), as colorless crystals, mp 81°C. *Anal.* Calcd for $C_{14}H_{10}N_4S$: C, 63.14; H, 3.78; N, 21.04. Found: C, 63.14; H, 3.82; N, 21.04.

(Benzothiazol-2-yl)(benzotriazole-1-yl)(phenylthio)methane (19) was obtained by the reaction of **13** with **16**. The residue was triturated with diethyl ether (1×20 ml) to yield **19** (6.88g, 92%), as colorless crystals, mp 146-147°C. *Anal.* Calcd for $C_{20}H_{14}N_4S_2$: C, 64.15; H, 3.77; N, 14.96. Found: C, 63.99; H, 3.88; N, 14.97.

Crystallography

Crystal data for 9 at -143°C: $C_{17}H_{16}N_4S_2$, Mr = 340.5, monoclinic, space group $P2_1/c$, a = 11.682(2), b = 19.071(4), c = 7.615(2) Å, β = 108.02(1)°, U = 1613(6) Å^3, F(000) = 712, Z = 4, D_c = 1.40 g cm^{-3}, μ(Mo-Kα) = 3.34 cm^{-1}, 0.65 x 0.41 x 0.11 mm, ω scans, $2\theta_{max}$ = 48°, N = 2507, 208 parameters, S = 1.04, wR(F^2) = 0.117, R = 0.043 for 1979 reflections with $I > 2\sigma(I)$.

Crystal data for 10 at -143°C: $C_{21}H_{13}N_5S_3$, Mr = 431.5, orthorhombic, space group $P2_12_12_1$, a = 9.671(2), b = 10.236(2), c = 19.311(4) Å, β = 108.02(1)°, U = 1911.6(7) Å^3, F(000) = 888, Z = 4, D_c = 1.50 g cm^{-3}, μ(Mo-Kα) = 4.07 cm^{-1}, 0.76 x 0.19 x 0.05 mm, ω scans, $2\theta_{max}$ = 52°, N = 2153, 262 parameters, S = 0.87, wR(F^2) = 0.078, R = 0.038 for 1649 reflections with $I > 2\sigma(I)$.

Intensity data were collected at -143°C with a Nicolet R3m four-circle diffractometer by using monochromatized Mo Kα (λ = 0.7107Å) radiation. Cell parameters were determined by least square refinements, the setting angles of >25 accurately centered reflections (2θ > 25) being used. Throughout data collections the intensities of three standard reflections were monitored at regular intervals and this indicated no significant crystal decomposition. The space groups followed from systematic absences. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The structures were solved by direct methods, and refined on F^2 using SHELXL92. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.3 times the isotropic equivalent of their carrier carbons. The function minimized was $\Sigma w(F_o^2-F_c^2)$, with $w = [\sigma^2(f_o^2) + 0.0624P^2 + 1.106P]^{-1}$ for **9** and $w = [\sigma^2(f_o^2) + 0.0378P^2]^{-1}$ for **10**, where $P = [\max(F_o^2 + 2F_c^2]/3$. Final atom coordinates, bond lengths and bond angles are listed in Tables 2-5. Tabulations of hydrogen atom coordinates, anisotropic thermal parameters, structure factors and equations of meanplanes are available from the author P.J.S.

Table 2. Atomic coordinates (x10^4) and isotropic thermal parameters (Å^{2}x10^3) for **9**.

	x	y	z	U_{eq} [a]
C(1)	1448(3)	3264(2)	-746(4)	24(1)
S(2)	1964(1)	3595(1)	1592(1)	26(1)
C(1')	3534(3)	3341(2)	2268(5)	39(1)
C(2')	4414(4)	3766(2)	1739(8)	84(2)
C(3')	4458(5)	4453(3)	1926(12)	137(3)
N(1)	1820(2)	3688(1)	-2067(3)	23(1)
N(2)	2592(2)	3400(1)	-2899(4)	32(1)
N(3)	2875(2)	3874(2)	-3915(4)	37(1)
C(3A)	2285(3)	4487(2)	-3760(4)	28(1)
C(4)	2294(3)	5144(2)	-4568(4)	37(1)
C(5)	1613(3)	5659(2)	-4162(4)	34(1)
C(6)	932(3)	5540(2)	-2953(4)	31(1)
C(7)	913(3)	4901 (1)	-2141(4)	26(1)
C(7A)	1610(2)	4374(1)	-2569(4)	21(1)
S(1')	-611(1)	2475(1)	-2524(1)	30(1)
C(2')	103(3)	3207(1)	-1309(4)	22(1)
N(3')	-581(2)	3680(1)	-964(3)	21(1)
C(3A')	-1779(2)	3487(1)	-1679(4)	23(1)
C(4')	-2755(3)	3889(2)	-1568(4)	31(1)
C(5')	-3892(3)	3631(2)	-2389(4)	38(1)
C(6')	-4070(3)	2981(2)	-3262(4)	42(1)
C(7')	-3128(3)	2577(2)	-3371(4)	38(1)
C(7A')	-1976(3)	2836(2)	-2571(4)	28(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 3. Atomic coordinates (x10^4) and isotropic thermal parameters (Å^{2}x10^3) for **10.**

	x	y	z	U_{eq} [a]
C(1)	574(4)	8812(4)	2455(2)	16(1)
S(1)	1824(1)	7848(1)	1977(1)	18(1)
N(1)	-818(4)	8255(3)	2425(2)	14(1)
N(2)	-1073(4)	7074(3)	2724(2)	19(1)
N(3)	-2405(4)	6866(4)	2736(2)	19(1)
C(3A)	-3045(5)	7965(4)	2456(2)	17(1)
C(4)	-4453(5)	8259(4)	2366(2)	21(1)
C(5)	-4773(4)	9428(4)	2068(2)	21(1)
C(6)	-3737(4)	10314(4)	1854(2)	18(1)
C(7)	-2350(4)	10045(4)	1936(2)	15(1)
C(7A)	-2034(4)	8858(4)	2259(2)	14(1)
S(1')	38(1)	9897(1)	3761(1)	23(1)
C(2')	1018(4)	8908(4)	3203(2)	16(1)
N(3')	2004(4)	8247(3)	3479(2)	18(1)
C(3A')	2047(5)	8465(4)	4199(2)	17(1)
C(4')	2983(5)	7887(4)	4652(2)	24(1)
C(5')	2846(5)	8169(4)	5355(2)	26(1)
C(6')	1820(5)	8999(4)	5596(2)	23(1)
C(7')	911(5)	9599(4)	5154(2)	22(1)
C(7A')	1030(5)	9316(4)	4447(2)	19(1)
S(1")	2044(1)	7514(1)	434(1)	25(1)
C(2")	1248(4)	8285(4)	1141(2)	17(1)
N(3")	301(4)	9119(3)	1013(2)	18(1)
C(3A")	124(5)	9242(4)	292(2)	20(1)
C(4")	-790(5)	10090(5)	-32(2)	27(1)
C(5")	-818(6)	10124(5)	-747(3)	36(1)
C(6")	39(6)	9317(5)	-1144(2)	40(1)
C(7")	965(6)	8473(5)	-831(2)	34(1)
C(7A")	977(5)	8442(4)	-109(2)	25(1)

Table 4. Bond lengths (Å) and angles (°) for **9**.

C(1)-N(1)	1.458(3)	C(1)-C(2')	1.499(4)	C(1)-S(2)	1.808(3)
S(2)-C(1')	1.811(3)	C(1')-C(2')	1.460(5)	C(2')-C(3')	1.318(6)
N(1)-C(7A)	1.365(4)	N(1)-N(2)	1.367(3)	N(2)-N(3)	1.297(4)
N(3)-C(3A)	1.379(4)	C(3A)-C(7A)	1.391(4)	C(3A)-C(4)	1.399(4)
C(4)-C(5)	1.359(5)	C(5)-C(6)	1.409(4)	C(6)-C(7)	1.370(4)
C(7)-C(7A)	1.393(4)	S(1')-C(7A')	1.727(3)	S(1')-C(2')	1.739(3)
C(2')-N(3')	1.286(4)	N(3')-C(3A')	1.385(4)	C(3A')-C(4')	1.396(4)
C(3A')-C(7A')	1.402(4)	C(4')-C(5')	1.374(4)	C(5')-C(6')	1.391(5)
C(6')-C(7')	1.367(5)	C(7')-C(7A')	1.386(4)		

N(1)-C(1)-C(2')	110.7(2)	C(7')-C(7A')-S(1')	129.1(3)	N(1)-C(1)-S(2)	114.0(2)
C(2')-C(1)-S(2)	108.0(2)	C(6')-C(7')-C(7A')	117.6(3)	C(1)-S(2)-C(1')	100.8(2)
C(2')-C(1')-S(2)	120.7(3)	C(4')-C(5')-C(6')	121.2(3)	C(3')-C(2')-C(1')	121.9(5)
C(7A)-N(1)-N(2)	110.1(2)	C(4')-C(3A')-C(7A')	120.1(3)	C(7A)-N(1)-C(1)	131.2(2)
N(2)-N(1)-C(1)	118.6(2)	N(3')-C(3A')-C(4')	125.2(3)	N(3)-N(2)-N(1)	108.8(2)
N(2)-N(3)-C(3A)	108.3(2)	C(1)-C(2')-S(1')	119.9(2)	N(3)-C(3A)-C(7A)	108.9(3)
N(3)-C(3A)-C(4)	130.5(3)	C(2')-N(3')-C(3A)	110.6(2)	C(7A)-C(3A)-C(4)	120.5(3)
C(5)-C(4)-C(3A)	117.6(3)	N(3)-C(3A)-C(7A')	114.7(3)	C(4)-C(5)-C(6)	121.5(3)
C(7)-C(6)-C(5)	122.0(3)	C(5')-C(4')-C(3A')	118.0(3)	C(6)-C(7)-C(7A)	116.3(3)
N(1)-C(7A)-C(3A)	103.9(2)	C(7')-C(6')-C(5')	121.8(3)	N(1)-C(7A)-C(7)	134.0(3)
C(3A)-C(7A)-C(7)	122.1(3)	C(7')-C(7A')-C(3A')	121.4(3)	C(7A')-S(1')-C(2')	88.7(1)
N(3')-C(2')-C(1)	123.6(2)	C(3A')-C(7A')-S(1')	109.5(2)	N(3')-C(2')-S(1')	116.5(2)

Table 5. Bond lengths (Å) and angles (°) for **10**.

C(1)-N(1)	1.462(5)	C(1)-C(2')	1.511(6)	C(1)-S(1)	1.813(4)
S(1)-C(2")	1.766(4)	N(1)-N(2)	1.362(5)	N(1)-C(7A)	1.366(5)
N(2)-N(3)	1.306(5)	N(3)-C(3A)	1.392(5)	C(3A)-C(7A)	1.392(6)
C(3A)-C(4)	1.406(6)	C(4)-C(5)	1.363(6)	C(5)-C(6)	1.413(6)
C(6)-C(7)	1.379(6)	C(7)-C(7A)	1.400(6)	S(1')-C(7A')	1.740(4)
S(1')-C(2')	1.756(4)	C(2')-N(3')	1.285(5)	N(3')-C(3A')	1.410(5)
C(3A')-C(4')	1.391(6)	C(3A')-C(7A')	1.398(6)	C(4')-C(5')	1.393(6)
C(5')-C(6')	1.387(6)	C(6')-C(7')	1.371(6)	C(7')-C(7A')	1.400(6)
S(1")-C(7A")	1.751(5)	S(1")-C(2")	1.755(4)	C(2")-N(3")	1.276(5)
N(3")-C(3A")	1.409(5)	C(3A")-C(4")	1.387(6)	C(3A")-C(7A")	1.396(6)
C(4")-C(5")	1.383(6)	C(5")-C(6")	1.398(7)	C(6")-C(7") 1.384(7)	
C(7")-C(7A")	1.394(6)				

N(1)-C(1)-C(2')	108.9(3)	C(3A')-C(7A')-S(1')	109.9(3)	N(1)-C(1)-S(1)	112.5(3)
C(2')-C(1)-S(1)	109.4(3)	C(7A")-S(1")-C(2")	87.9(2)	C(2")-S(1)-C(1)	96.7(2)
N(2)-N(1)-C(7A)	110.1(3)	N(3")-C(2")-S(1)	124.9(3)	N(2)-N(1)-C(1)	119.8(3)
C(7A)-N(1)-C(1)	128.7(3)	C(2")-N(3")-C(3A")	109.8(4)	N(3)-N(2)-N(1)	109.3(4)
N(2)-N(3)-C(3A)	107.4(4)	C(4")-C(3A")-N(3")	125.3(4)	C(7A)-C(3A)-N(3)	109.0(4)
C(7A)-C(3A)-C(4)	120.4(4)	C(5")-C(4")-C(3A")	118.6(5)	N(3)-C(3A)-C(4)	130.6(4)
C(5)-C(4)-C(3A)	117.4(4)	C(7")-C(6")-C(5")	120.9(4)	C(4)-C(5)-C(6)	121.8(4)
C(7)-C(6)-C(5)	121.9(4)	C(7")-C(7A")-C(3A")	122.4(5)	C(6)-C(7)-C(7A)	115.9(4)
N(1)-C(7A)-C(3A)	104.1(3)	C(7')-C(7A')-S(1')	128.8(4)	N(1)-C(7A)-C(7)	133.2(4)
C(3A)-C(7A)-C(7)	122.6(4)	N(3")-C(2")-S(1")	117.7(3)	C(7A')-S(1')-C(2')	88.4(2)
N(3')-C(2')-C(1)	125.0(4)	S(1")-C(2")-S(1)	117.3(2)	N(3')-C(2)-S(1')	116.7(3)
C(1)-C(2')-S(1')	118.1(3)	C(4")-C(3A")-C(7A")	119.6(4)	C(2')-N(3')-C(3A')	110.3(4)
C(4')-C(3A')-C(7A')	120.5(4)	C(7A")-C(3A")-N(3")	115.1(4)	C(4')-C(3A')-N(3')	124.9(4)
C(7A')-C(3A')-N(3')	114.5(4)	C(4")-C(5")-C(6")	121.4(5)	C(3A')-C(4')-C(5')	117.5(4)
C(6')-C(5')-C(4')	121.5(4)	C(6")-C(7")-C(7A")	117.1(5)	C(7')-C(6')-C(5')	121.6(4)
C(6')-C(7')-C(7A')	117.5(4)	C(7")-C(7A")-S(1")	128.0(4)	C(3A')-C(7A')-C(7')	121.3(4)
C(3A")-C(7A")-S(1")	109.6(3)				

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REFERENCES

1. A. R. Katritzky, J. M. Aurrecoechea, and L. M. Vazquez de Miguel, *J. Chem. Soc., Perkin Trans. 1*, **1987**, 769.
2. A. R. Katritzky, W. Kuzmierkiewicz, and J. M. Aurrecoechea, *J. Org. Chem.*, **1987**, *52*, 844.
3. A. R. Katritzky, H. Lang,and X. Lan, *Tetrahedron*, **1993**, *49*, 2829, and references therein.
4. A. R. Katritzky, X. Lan,and J. N. Lam, *Chem. Ber.*, **1991**, *124*, 1819.
5. A. R. Katritzky and J. N. Lam, *Heteroatom Chemistry*, **1990**, *1*, 21.
6. A. R. Katritzky, X. Zhao,and I. V. Shcherbakova, *J. Chem. Soc., Perkin. Trans. 1*, **1991**, 3295.
7. A. R. Katritzky, S. Perumal, W. Kuzmierkiewicz, P. Lue, and J. V. Greenhill, *Helv. Chim. Acta*, **1991**, *74*, 1924.
8. A. R. Katritzky, S. Rachwal, and K. C. Caster, *J. Chem. Soc., Perkin. Trans. 1*, **1987**, 781.

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