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Homochiral Cycloadducts Derived from Sugar Aldoximes *via* Nitrone Intermediates

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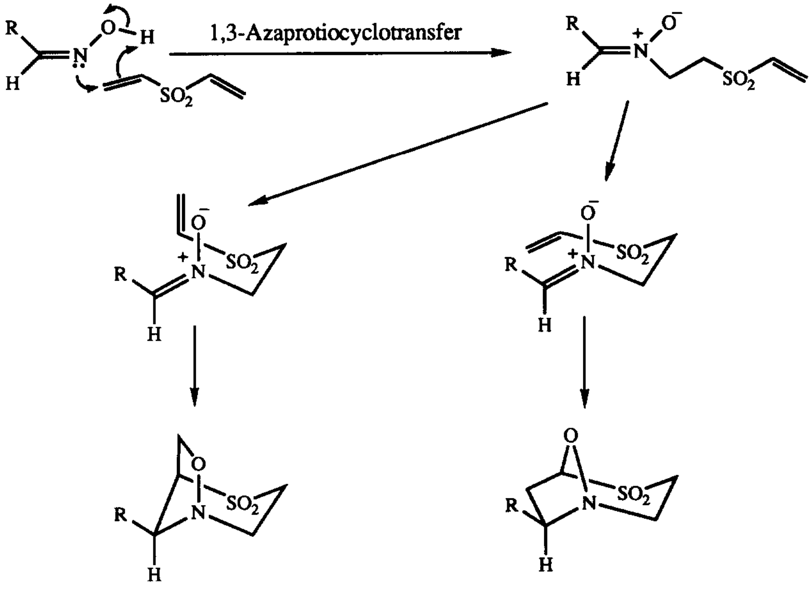
Abstract: Tandem nitrone generation/cycloaddition reactions between simple sugar aldoximes and divinyl sulphone in refluxing toluene have been shown to occur regiospecifically and with high diastereoselectivity in the cycloaddition step to afford homochiral cycloadducts in good yield. The process is applicable to both furanose and pyranose aldoximes. Absolute stereochemistries of the products have been determined by NOE spectroscopy and X-ray crystallography.

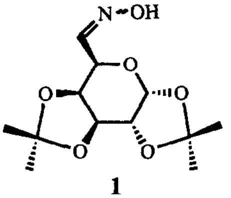
As part of our ongoing research into the use of simple oximes in the synthesis of heterocyclic systems *via* intermediate nitrone species, we are exploring the applicability of our 1,3-azaprotiocyclotransfer (APT)-cycloaddition cascades[1] to the synthesis of homochiral cycloadducts from aldoximes obtained from readily accessible chiral materials. We report herein the results of our studies employing cyclic sugar aldoximes with divinyl sulphone as a bifunctional nitrone generation/dipolarophile species (Class 2 processes).[2,3] Our extensive previous work and studies herein indicate that the APT process results in formation of the thermodynamically more stable Z-nitrone.



Scheme

Reaction between an aldoxime and divinyl sulphone can result in the formation of products containing isomeric bicyclic structures, this potential non-specificity upon cycloaddition resulting from the fact that the nitrone intermediate can assume one of two possible pre-transition state conformations, (*Scheme*). Whilst aldoximes (R = phenyl or substituted phenyl) prefer to adopt a transition state conformation in which the oxygen atom of the nitrone adds to the less substituted end of the vinyl group, more sterically demanding aldoximes derived from substituted naphthalenes and ketoximes show much lower regioselectivity upon cycloaddition.[2] We were interested in the influence of aldoximes containing several contiguous chiral centres upon both regioselectivity and stereoselectivity in the cycloaddition step.

Oximes **1** and **2** were prepared from D-galactose[4] and D-ribose according to literature procedures as mixtures of geometric isomers, (*E*/*Z* ratios of 1:1 and 3:2 respectively). Oxime **2** could be separated into its component *E*- and *Z*- isomers by careful column chromatography on silica but was invariably used as an isomeric mixture in subsequent experiments.



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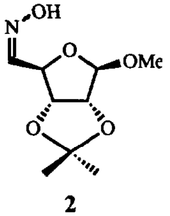
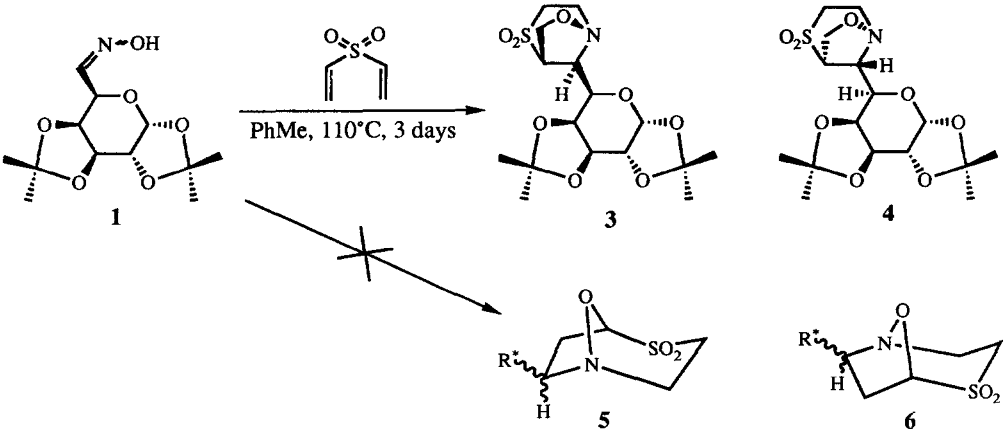
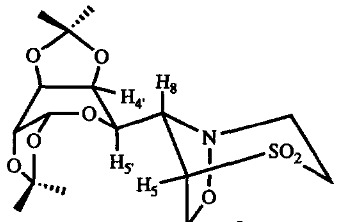


2

Reaction between oxime **1** and divinyl sulphone (1 equivalent) proceeded cleanly in toluene at 110°C over a three day period. ^{1}H nmr spectra of the crude reaction mixture showed the presence of two cycloadducts as evidenced by the appearence of two new doublets corresponding to the anomeric hydrogen of the pyranose ring, (isomeric ratio *ca.* 25:1). Careful column chromatography on silica allowed the separation of the major isomer **3** (86%) and a diastereomeric byproduct **4** (2%), (d.e. >95%).



Analysis of the ^{1}H nmr spectra of **3** and **4** showed that their structures differed only in the absolute stereochemistry within the newly formed 1-aza-7-oxa-4-thiadioxybicyclo[3·2·1]octane ring system due to cycloaddition at opposite diastereotopic faces of the intermediate nitrone. Compounds **5** and **6** derived from cycloaddition *via* regioisomeric transition states were not detected (nmr). The regiospecific cycloaddition is in accord with our previous studies on achiral oximes.[2]



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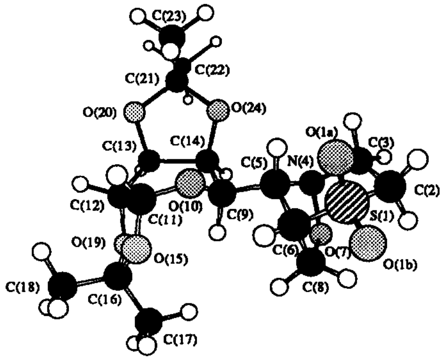
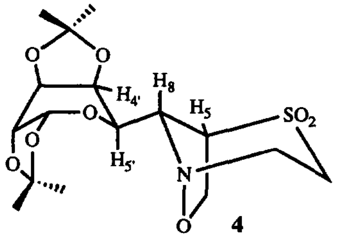
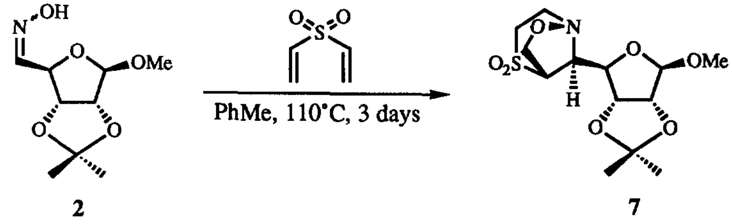


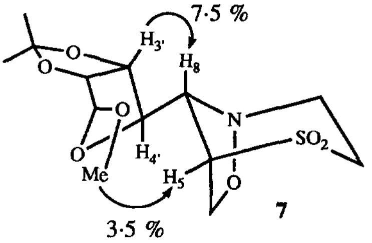
Figure: X-ray structure of **3**



4

Coupling constants allowed the determination of the solution structure of **3** at ambient temperature; the pyranose ring occurs in a twist-boat conformation with a dihedral angle between the two ring systems of *ca.* 180°, ($J_{5',8}$ 9.5Hz). The absolute stereochemistries of both **3** and **4** were assigned by a single crystal X-ray study[5] of **3** (*Figure*). This confirmed that cycloadduct **3** has *R*- configuration at the nitrogen atom; cycloadduct **4** therefore has *S*- stereochemistry at nitrogen.





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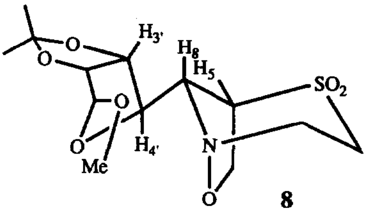

8

D-Ribosyl oxime **2** reacted with divinyl sulphone (1 equivalent) under identical conditions to afford a single cycloadduct (nmr). Column chromatography on silica afforded **7** as a colourless solid (52%) and nmr studies suggested that **7** had the same relative structure as **3** and **4**. Absolute stereochemistry within the newly formed bicycle of **7** was inferred by NOE spectroscopic measurements ($CDCl_3$) by careful examination of coupling constants, ($J_{4',8}$ 11Hz, antiperiplanar). Enhancement of H-8 (7·5%) and not of H-5 upon irradiation of H-3' together with an enhancement of H-5 (3·5%) upon irradiation of the anomeric methoxy signal was consistent only with the adduct **7** having the *R*- configuration about nitrogen. In this case the isomeric adduct **8** with *S*- stereochemistry at nitrogen that would result *via* cycloaddition at the opposite diastereotopic face of the nitrone intermediate was not found in the reaction mixture. The yield of cycloadduct is lower in this case due to the lower thermal stability of oxime **2** relative to **1**.

Cycloadducts **3**,**4** and **7** would appear to be derived from *Z*- oxime and since the yields of these adducts are greater than the initial *Z*- isomer content of oximes **1** and **2** it is apparent that thermal *E*/*Z* isomerization is occuring under the reaction conditions. It is believed that the APT process is rate limiting and that the activation energy for APT *via* the *Z*- oxime is lower than that for its *E*- isomer with thermal isomerization occuring rapidly at the oxime level possibly *via* an intermediate nitroso species. Evidence for *E*/*Z* interconversion was obtained when pure samples of both the *E*- and *Z*- isomers of oxime **2** were heated at 110°C in d_8-toluene. Monitoring of the mixtures over 24 hours by nmr showed that isomerization had occured in each sample to afford a 2:1 *E*/*Z* mixture of **2**. Under acidic conditions the isomerization was found to be far more facile. Thus isomerization of *E*- and *Z*- **2** occured readily in $CDCl_3$ (traces of HCl present) at room temperature. Within 20 minutes pure samples of *E*- and *Z*- oxime showed signs of isomerization and eventually equilibrated to a 3:2 *E*/*Z* mixture.

The reasons for such high diastereoselectivities in these reactions is the subject of continuing research. Work is also in progress to extend this approach to other readily available chiral oximes derived from acyclic sugars, terpenes and amino acids.

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EXPERIMENTAL

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Specific rotations were measured at ambient temperature with an Optical Activity Ltd., AA-1000 polarimeter. Microanalyses were obtained using a Carbo Erba MOD 1106 instrument. Fast atom bombardment mass spectra were recorded with a VG Autospec mass spectrometer using caesium as the ionizing agent. Infrared spectra were recorded on a Perkin Elmer 1310 spectrophotometer as a thin film or as a nujol mull as indicated. Nuclear magnetic resonance spectra were recorded on a Bruker AM400 spectrometer operating at 400·1 MHz (^{1}H) and 100·6 MHz (^{13}C) in the solvents specified. Flash column chromatography was performed using silica gel 60 (Merck 9385). Petroleum ethers (b.p. 40-60°C and b.p. 60-80°C) were distilled prior to use.

Methyl 2,3-*O*-isopropylidene-β-D-*ribo*-pentodialdo-1,4-furanose oxime 2. A solution of methyl 2,3-*O*-isopropylidene-β-D-*ribo*-pentodialdo-1,4-furanose[6] (2·47 g, 12·23 mmol) in pyridine (2 ml, 24·76 mmol), methanol (10 ml) and water (2 ml) was treated with hydroxylamine hydrochloride (1·00 g, 14·39 mmol) according to a published procedure for the synthesis of oxime **1**[4] to afford methyl 2,3-*O*-isopropylidene-β-D-*ribo*-pentodialdo-1,4-furanose oxime (*E*/*Z* 3:2) **2** as a cloudy colourless oil, (1·91 g, 72%). Distillation in a Kugelrohr apparatus afforded a colourless oil, b.p. 180-5°C, (0·7 mmHg). $[\alpha]_D$ -125·6° (*c* 0·5, $CHCl_3$); (Found: C, 49·55; H, 7·0; N, 6·7. $C_9H_{15}NO_5$ requires C, 49·75; H, 6·95; N, 6·45%); *m*/*z* (%) 257 (MH^+, 57); ν_{max} (film) 3340, 1630cm^{-1}; δ_H ($CDCl_3$) 7·38 (1H, d, *J* 6·5 Hz, H-5), 6·80 (1H, d, *J* 4·5 Hz, H-5'), 5·23 (1H, dt, *J* 4·5, 1 Hz, H-4'), 5·05 (1H, s, H-1 or H-1'), 5·01 (1H, s, H-1' or H-1), 4·90 (1H, d, *J* 6 Hz, H-2 or H-2'), 4·85 (1H, dd, *J* 6.5, 0·5 Hz, H-4), 4·62 (1H, d, *J* 6 Hz, H-2' or H-2), 4·56 (1H, dd, *J* 6, 0·5 Hz, H-3), 3·41 (3H, s, OMe or OMe'), 3·34 (3H, s, OMe' or OMe), 1·50, 1·49, 1·33 and 1·32 (4x3H, 4xs, CMe_2 and CMe_2'); δ_C ($CDCl_3$) 152·5 (C-5'), 150·4 (C-5), 112·7 and 112·6 ($\mathit{C}Me_2$ and $\mathit{C}Me_2$'), 109·7 and 109·3 (C-1 and C-1'), 85·1 (C-2 or C-2'), 84·4 (C-3), 83·5 and 83·4 (C-3' and C-4), 82·6 (C-2' or C-2), 81·5 (C-4'), 55·1 and 54·9 (OMe and OMe'), 26·3, 26·3, 25·0 and 24·9 ($C\mathit{Me}_2$ and $C\mathit{Me}_2$').

1(*R*),5(*S*),5'(*R*),8(*S*)-8-[5'-(1',2':3',4'-di-*O*-isopropylidene-α-L-*arabino*-pyranosidyl)]-1-aza-7-oxa-4-thiadioxybicyclo[3.2.1]octane 3. A solution of 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose oxime **1** (273 mg, 1·00 mmol) and divinyl sulphone (118 mg, 1·00 mmol) in toluene (8 ml) was stirred and held at reflux for three days. Upon cooling the solvent was removed *in vacuo* and the residue was subjected to column chromatography on silica. Elution with petroleum ether (b.p. 40-60°C) and diethyl ether 1:3 afforded the *title compound* **3** (338 mg, 86%), R_f 0·25, as a colourless solid that crystallized from petroleum ether (b.p. 60-80°C) and chloroform as colourless prisms, m.p. 238°C (decomp.). $[\alpha]_D$ -89·6° (*c* 0·5, $CHCl_3$); (Found: C, 48·95; H, 6·45; N, 3·4; S, 8·3. $C_{16}H_{25}NO_8S$ requires C, 49·1; H, 6·45; N, 3·6; S, 8·2%); *m/z* (%) 392 (MH^+, 100); ν_{max} (nujol) 1315, 1120 cm^{-1}; δ_H ($CDCl_3$) 5·49 (1H, d, *J* 5 Hz, H-1'), 4·60 (1H, dd, *J* 8, 2·5 Hz, H-3'), 4·50 (1H, d, *J* 9·5 Hz, H-6α), 4·39 (1H, dd, *J* 8, 2 Hz, H-4'), 4·37 (1H, d, *J* 9·5 Hz, H-8), 4·31 (1H, dd, *J* 5, 2·5 Hz, H-2'), 4·12 (1H, dd, *J* 6, 3 Hz, H-5), 4·05 (1H, dd, *J* 9·5, 6 Hz, H-6β), 3·61 (1H, m, H-2β), 3·47 (1H, dd, *J* 9·5, 2 Hz, H-5'), 3·32 (2H, m, H-2α and H-3β), 2·99 (1H, m, H-3α), 1·45 (3H, s, Me), 1·44 (3H, s, Me), 1·33 (3H, s, Me), 1·30 (3H, s, Me); δ_C ($CDCl_3$) 109·6 ($\mathit{C}Me_2$), 108·7 ($\mathit{C}Me_2$), 96·5 (C-1'), 70·7 (C-2' and C-3'), 70·2 (C-4' or C-8), 68·7 (C-6), 67·6 (C-8 or C-4'), 64·7 (C-5'), 64·3 (C-5), 53·5 (C-2), 46·3(C-3), 26·0, 26·0, 24·8 and 24·5 ($C\mathit{Me}_2$ and $C\mathit{Me}_2$).

1(*R*),5(*S*),4'(*R*),8(*S*)-8-[4'-(methyl 2,3-*O*-isopropylidene-β-D-*erythro*-furanosidyl)]-1-aza-7-oxa-4-thiadioxybicyclo[3.2.1]octane 7. A solution of methyl 2,3-*O*-isopropylidene-β-D-*ribo*-pentodialdo-1,4-furanose oxime **2** (217 mg, 1·00 mmol) and divinyl sulphone (118 mg, 1·00 mmol) in toluene (8 ml) was stirred and held at reflux for three days. Upon cooling the solvent was removed *in vacuo* and the residue was subjected to column chromatography on silica. Elution with petroleum ether (b.p. 40-60°C) and diethyl ether 1:3 afforded the *title compound* **7** (175 mg, 52%), R_f 0·30, as a colourless solid that crystallized from petroleum ether (b.p. 60-80°C) and chloroform as colourless prisms, m.p. 170°C (decomp.). $[\alpha]_D$ -40·0° (*c* 0·5, $CHCl_3$); (Found: C, 46·55; H, 6·45; N, 4·35; S, 9·4. $C_{13}H_{21}NO_7S$ requires C, 46·55; H, 6·3; N, 4·2; S, 9·55%); *m/z* (%) 336 (MH^+, 57), 304 (M^+-OMe, 100); ν_{max} (nujol) 1310, 1120 cm^{-1}; δ_H ($CDCl_3$) 5·01 (1H, s, H-1'), 4·86 (1H, d, *J* 6 Hz, H-3'), 4·64 (1H, d, *J* 6 Hz, H-2'), 4·54 (1H, *J* 10 Hz, H-6α), 4·21 (1H, dd, *J* 10, 5·5 Hz, H-6β), 4·04 (1H, dd, *J* 5·5, 3 Hz, H-5), 4·02 (1H, d, *J* 11 Hz, H-8), 3·85 (1H, d, *J* 11 Hz, H-4'), 3·66 (1H, dd, *J* 14, 5·5 Hz, H-2β), 3·42 (3H, s, OMe), 3·36 (1H, ddd, *J* 14, 12, 5·5 Hz, H-3β), 3·24 (1H, ddd, *J* 14, 12, 4·5 Hz, H-2α), 3·02 (1H, ddd, *J* 14, 4·5, 3 Hz, H-3α), 1·46 (3H, s, Me), 1·31 (3H, s, Me); δ_C ($CDCl_3$) 112·6 ($\mathit{C}Me_2$), 109·9 (C-1'), 84·7 (C-2'), 83·3 (C-4'), 82·4 (C-3'), 71·1 (C-8), 68·7 (C-6), 64·7 (C-5), 55·8 (OMe), 53·6 (C-2), 46·2 (C-3), 26·2 and 24·7 ($C\mathit{Me}_2$).

Single crystal X-ray diffraction analysis of 3. All crystallographic measurements were carried out at ambient temperature on a Stoe STAD14 diffractometer using graphite monochromated Copper K_α X-radiation (λ=1·54184 Å). Two equivalent sets of data were collected in the range 4·0°<2θ<130° using ω/θ scans. No significant variation was observed in the intensity of five standard reflections. Lorentz and polarisation corrections were applied to the data-set together with a semi-empirical absorption correction based on azimuthal ψ-scans. The structure was solved by direct methods using SHELXS-86[7] and was refined by full-matrix least squares (based on F^2) using SHELXL-93[8] which uses all data for refinement. The weighting scheme was $\omega = [\sigma^2(F_0{}^2) + (0{\cdot}0454P)^2 + 0{\cdot}2506P]^{-1}$ where $P = (F_0{}^2+2F_c{}^2)/3$. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were constrained to predicted positions (C-H = 0·96, 0·97 and 0·98Å for primary, secondary and tertiary hydrogens respectively). Non-hydrogen atomic co-ordinates, bond lengths and bond angles are listed in Tables 1-3. Supplementary data, which includes hydrogen co-ordinates and all thermal parameters together with complete bond lengths and angles, has been deposited at the Cambridge Crystallographic Data Centre and is available on request.

Table 1. Non-hydrogen atom co-ordinates (x 10^4) and equivalent isotropic thermal parameters (Å^2 x 10^3) for 3 with estimated standard deviations (e.s.d.'s) in parentheses.

Atom	x	y	z	U_{eq}*
S(1)	7470·4(6)	7446·1(7)	623·72(14)	41·3(2)
O(1a)	6452(2)	6489(2)	552·9(5)	58·5(6)
O(1b)	7201(2)	8800(2)	537·7(5)	63·8(7)
C(2)	8939(3)	9647(3)	396·6(6)	45·9(7)
C(3)	9618(3)	5786(3)	587·5(6)	44·9(6)
N(4)	9702(2)	5823(2)	992·4(5)	33·8(5)
C(5)	8399(2)	5876(2)	1162·5(5)	27·2(5)
C(6)	7973(2)	7297(2)	1093·0(5)	30·8(5)
O(7)	10281(2)	7073(2)	1093·5(5)	45·1(5)
C(8)	9249(3)	8025(3)	1159·6(7)	41·2(6)
C(9)	8444(2)	5535(2)	1572·4(5)	27·8(5)
O(10)	7090(2)	5386(2)	1677·9(4)	34·6(4)
C(11)	6882(3)	5326(3)	2061·8(6)	42·2(6)
C(12)	7991(3)	4646(3)	2278·9(6)	39·9(6)
C(13)	8890(3)	3779(3)	2052·3(6)	38·1(6)
C(14)	9200(2)	4297(2)	1656·1(6)	31·0(5)
O(15)	6829(2)	6615(2)	2210·7(5)	58·1(6)
C(16)	7828(3)	6779(3)	2486·8(6)	47·2(7)
C(17)	8533(3)	8076(3)	2425·9(8)	59·2(8)
C(18)	7188(3)	6668(4)	2867·5(7)	61·7(9)
O(19)	8731(2)	5735(2)	2420·6(4)	38·3(4)
O(20)	8226(2)	2573(2)	1992·1(5)	55·8(5)
C(21)	8587(3)	2101(3)	1632·0(7)	45·5(7)
C(22)	9875(4)	1356(3)	1647·2(9)	63·0(9)
C(23)	7472(4)	1306(3)	1477·3(9)	67·8(9)
O(24)	8735(2)	3265(2)	1418·9(4)	39·8(4)

*U_{eq} = 1/3 x the trace of the orthoganalized U_{ij} matrix.

Table 2. Non-hydrogen bond lengths for **3** (Å).

S(1)-O(1b)	1·435(2)	S(1)-O(1a)	1·441(2)
S(1)-C(2)	1·775(3)	S(1)-C(6)	1·776(2)
C(2)-C(3)	1·529(4)	C(3)-N(4)	1·465(3)
N(4)-O(7)	1·446(3)	N(4)-C(5)	1·460(3)
C(5)-C(9)	1·520(3)	C(5)-C(6)	1·527(3)
C(6)-C(8)	1·510(4)	O(7)-C(8)	1·446(3)
C(9)-O(10)	1·434(3)	C(9)-C(14)	1·504(3)
O(10)-C(11)	1·404(2)	C(11)-O(15)	1·415(4)
C(11)-C(12)	1·536(3)	C(12)-O(19)	1·432(3)
C(12)-C(13)	1·509(4)	C(13)-O(20)	1·415(3)
C(13)-C(14)	1·556(3)	C(14)-O(24)	1·433(3)
O(15)-C(16)	1·432(3)	C(16)-O(19)	1·422(3)
C(16)-C(17)	1·515(5)	C(16)-C(18)	1·525(3)
O(20)-C(21)	1·433(3)	C(21)-O(24)	1·418(3)
C(21)-C(23)	1·499(4)	C(21)-C(22)	1·511(4)

Table 3. Non-hydrogen atom bond angles (°).

O(1b)-S(1)-O(1a)	118·05(14)	O(1b)-S(1)-C(2)	109·50(13)
O(1a)-S(1)-C(2)	109·15(14)	O(1b)-S(1)-C(6)	110·04(12)
O(1a)-S(1)-C(6)	108·54(10)	C(2)-S(1)-C(6)	100·04(11)
C(3)-C(2)-S(1)	113·0(2)	N(4)-C(3)-C(2)	117·1(2)
O(7)-N(4)-C(5)	103·3(2)	O(7)-N(4)-C(3)	107·4(2)
C(5)-N(4)-C(3)	111·6(2)	N(4)-C(5)-C(9)	112·0(2)
N(4)-C(5)-C(6)	102·8(2)	C(9)-C(5)-C(6)	112·5(2)
C(8)-C(6)-C(5)	101·2(2)	C(8)-C(6)-S(1)	110·9(2)
C(5)-C(6)-S(1)	108·6(2)	C(8)-O(7)-N(4)	109·5(2)
O(7)-C(8)-C(6)	105·6(2)	O(10)-C(9)-C(14)	110·3(2)
O(10)-C(9)-C(5)	104·7(2)	C(14)-C(9)-C(5)	113·6(2)
C(11)-O(10)-C(9)	114·3(2)	O(10)-C(11)-O(15)	109·9(2)
O(10)-C(11)-C(12)	114·4(2)	O(15)-C(11)-C(12)	104·5(2)
O(19)-C(12)-C(13)	109·0(2)	O(19)-C(12)-C(11)	102·7(2)
C(13)-C(12)-C(11)	115·4(2)	O(20)-C(13)-C(12)	107·4(2)
O(20)-C(13)-C(14)	104·3(2)	C(12)-C(13)-C(14)	115·1(2)
O(24)-C(14)-C(9)	108·9(2)	O(24)-C(14)-C(13)	103·6(2)
C(9)-C(14)-C(13)	111·4(2)	C(11)-O(15)-C(16)	110·2(2)
O(19)-C(16)-O(15)	104·6(2)	O(19)-C(16)-C(17)	108·6(2)
O(15)-C(16)-C(17)	109·6(2)	O(19)-C(16)-C(18)	111·8(2)
O(15)-C(16)-C(18)	108·5(2)	C(17)-C(16)-C(18)	113·4(2)
C(16)-O(19)-C(12)	107·3(2)	C(13)-O(20)-C(21)	107·9(2)
O(24)-C(21)-O(20)	103·9(2)	O(24)-C(21)-C(23)	109·1(2)
O(20)-C(21)-C(23)	108·9(3)	O(24)-C(21)-C(23)	110·2(2)
O(20)-C(21)-C(22)	110·9(2)	C(23)-C(21)-C(22)	113·4(3)
C(21)-O(24)-C(14)	108·7(2)		

Crystal data- $C_{16}H_{25}NO_8S$, 0·46 x 0·27 x 0·19 mm, M = 464·51, tetragonal, space group $P4_32_12$, $a=b$ = 10·1534(5), c = 36·104(2)Å, U = 3722·0(3)Å^3, Z = 8, D_x = 1·397 gcm^{-1}, μ = 1·941 mm^{-1}, $F(000)$ = 1664.

Data collection- Scan speeds 1·0-8·0 min^{-1}, ω scan widths 1·05°+α-doublet splitting, range 4·0<2θ<130·0°, 6329 data collected 3109 of which were unique, R_{int} = 0·0632, R_{sig} = 0·0642. There were 2597 reflections with $F_O > 4{\cdot}0\sigma(F_O)$.

Structure refinement- Number of parameters = 239. Goodness of fit s = 1·039, ωR_2 = 0·0914, R_1 = 0·0393.

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