Tricyclic Products from the Reaction between Penicillin derived Thiazoloazetidinones and Ethyl Diazoacetate. *X*-Ray Structure of Methyl 2-[(1*R*, 3*S*, 4*R*, 5*S*, 6*S*, 8*R*)-3-Benzyl-4,5-bismethoxycarbonyl-6-ethoxycarbonyl-9-oxo-7,10-diaza-2-thiatricyclo[6.2.0.0^{3,7}]decan-10-yl]-3-methylbut-2-enoate

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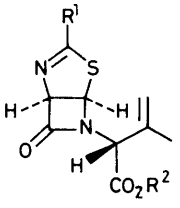
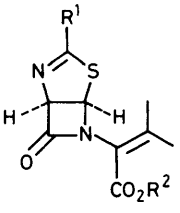
Treatment of methyl (2*R*)-2-[(1*R*, 5*R*)-3-benzyl-6-oxo-4,7-diaza-2-thiabicyclo[3.2.0]hept-3-en-7-yl]-3-methylbut-3-enoate (1; R^1 = $PhCH_2$, R^2 = Me) and its conjugated isomer (2; R^1 = $PhCH_2$, R^2 = Me) with an excess of ethyl diazoacetate in the presence of $Cu(acac)_2$ gave the tricyclic adducts methyl (2*R*)-2-[(1*R*, 3*S*, 4*R*, 5*S*, 6*S*, 8*R*)-3-benzyl-4,5,6-trisethoxycarbonyl-9-oxo-7,10-diaza-2-thiatricyclo[6.2.0.0^{3,7}]decan-10-yl]-3-methylbut-3-enoate (3) and (5), respectively. In the presence of dimethyl fumarate the analogous 4,5-bismethoxycarbonyl adducts (4) and (6) were also obtained. The structure of methyl 2-[(1*R*, 3*S*, 4*R*, 5*S*, 6*S*, 8*R*)-3-benzyl-4,5-bismethoxycarbonyl-6-ethoxycarbonyl-9-oxo-7,10-diaza-2-thiatricyclo[6.2.0.0^{3,7}]decan-10-yl]-3-methylbut-2-enoate (6) was established by an *X*-ray structure determination.

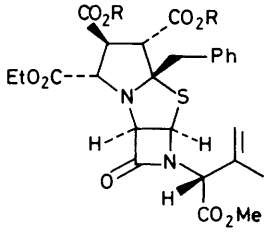
SINCE they were first prepared from penicillins,[1] thiazoloazetidinones (1) and (2) have become important intermediates in syntheses of β-lactam antibiotic analogues.[2] One feature of the chemistry of thiazoloazetidinones (1) is the unreactivity of the non-conjugated double-bond towards electrophilic attack; soft electrophiles prefer to attack at sulphur,[3,4] hard electrophiles at the thiazoline nitrogen.[5] We here describe reactions between thiazoloazetidinones (1) and (2) and carbenes and carbenoids. Several useful reactions have already been developed between carbenes and carbenoids and penams and cephems.[6] In our case, attack by the carbenoid on the thiazoline sulphur would give a sulphur ylide,



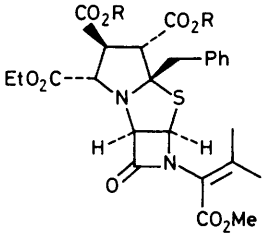
(1)



(2)



(3) R = Et
(4) R = Me



(5) R = Et
(6) R = Me

which should rearrange *via* a 1,2-shift to give intermediates of use for carbapenam synthesis. Alternatively, if attack occurred on the double-bond, products of use in penicillin homologue synthesis would be obtained.

RESULTS AND DISCUSSION

Preliminary studies of reactions between thiazoloazetidinones (1; R^1 = $PhCH_2$, R^2 = Me) and (2; R^1 = $PhCH_2$, R^2 = Me), prepared as described by Cooper,[1] and dibromocarbene generated from phenyltribromomethylmercury in refluxing benzene,[7] were not encouraging. Large excesses of carbene precursor were required to cause significant disappearance of starting thiazoloazetidinone and only very low yields of complex mixtures of products were obtained after column chromatography. However, treatment of the non-conjugated thiazoloazetidinone (1; R^1 = $PhCH_2$, R^2 = Me) with an excess of ethyl diazoacetate in the presence of a catalytic amount of $Cu(acac)_2$ led to more promising results. Column chromatography of the crude product mixture gave diethyl fumarate and diethyl maleate, a small amount of unchanged thiazoloazetidinone, and a single major product isolated in 45% yield after chromatography. It was not possible to identify the product solely on the basis of its spectroscopic data. ^{1}H N.m.r. spectroscopy showed the presence of three ethyl ester groups suggesting that three ethoxycarbonylcarbene units had been incorporated, and this was confirmed by the mass spectrum (M^+ 588). The ^{1}H n.m.r. spectrum also showed that the β-lactam nitrogen substituent [$CH(CO_2Me)\cdot CMe = CH_2$] was unchanged, and that the β-lactam was still *cis*-substituted by N- and S-substituents (two doublets, δ 5.34, 6.01; *J* 4 Hz). When the reaction was repeated in the presence of dimethyl fumarate, a second product was isolated (17%) which appeared to have incorporated one ethoxycarbonylcarbene unit, and one molecule of dimethyl fumarate (peaks due

to one ethyl and three methyl esters present in the ^{1}H n.m.r.; M^+ 560).

Similar results were obtained with the conjugated thiazoline (2; $R^1 = PhCH_2$, $R^2 = Me$). Thus treatment with an excess of ethyl diazoacetate and $Cu(acac)_2$ gave a single major product which had incorporated three ethoxycarbonylcarbene units, whereas addition of dimethyl fumarate to the reaction mixture gave a second product which had incorporated one molecule of dimethyl fumarate, and one ethoxycarbonylcarbene unit.

The structures of these products were solved by an *X*-ray diffraction study. In particular, the structure of the product from the conjugated thiazoline (2; $R^1 = PhCH_2$, $R^2 = Me$) and ethyl diazoacetate, in the presence of dimethyl fumarate, was shown to be the tricyclic adduct (6). The Figure shows a computer drawn rep-

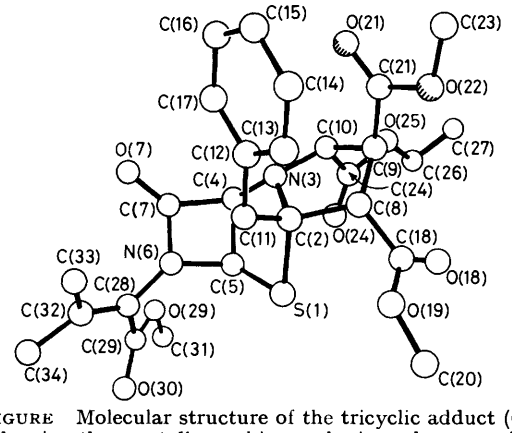
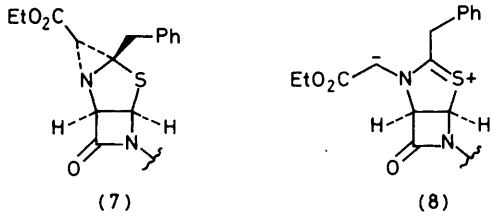


FIGURE Molecular structure of the tricyclic adduct (6) showing the crystallographic numbering scheme used

resentation of the molecule, which establishes the structure and indicates the stereochemistry of the new chiral centres. By analogy, and by comparison of the adduct ^{1}H n.m.r. spectra, the product obtained in the absence of dimethyl fumarate was identified as the trisethoxycarbonylcarbene adduct (5).

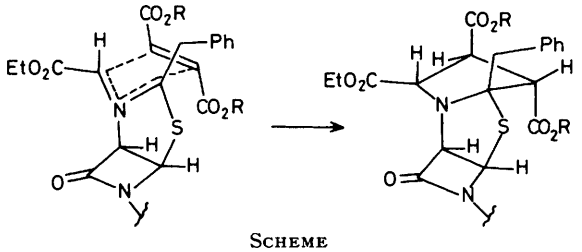
The products from the nonconjugated thiazoline (1; $R^1 = PhCH_2$, $R^2 = Me$) were correspondingly identified as adducts (3) (no dimethyl fumarate present) and (4). The configurations of the new chiral centres in adducts (3) and (4) were not unambiguously established. However, treatment of the non-conjugated trisethoxycarbonyl carbene adduct (3) with triethylamine gave the conjugated isomer (5) quantitatively, no other isomers being detected. This suggests that the configurations of the new chiral centres in adduct (3) are the same as those in adduct (5).

The adducts (3)—(6) would appear to have been formed *via* initial attack of the ethoxycarbonylcarbenoid on the C=N system to give either the aziridine (7) or the ylide (8). Cycloaddition of the ylide (8) on either diethyl or dimethyl fumarate would account for the observed products. The stereochemistry at C-3 is consistent with approach of the fumarate ester from the less hindered side of the ylide, and, although the mechanistic details of the processes involved were not examined, the reactions would appear to be quite stereoselective since appreciable quantities of other isomers could not be detected in the crude reaction mixtures (see Scheme). Reactions between carbenes and carbenoids, and imines,[8]



and related heterocycles,[9] are well known. In some cases aziridines have been isolated,[10] whereas in other cases nitrogen ylides are postulated as intermediates.[11]

Thus thiazolines (1; $R^1 = PhCH_2$, $R^2 = Me$) and (2; $R^1 = PhCH_2$, $R^2 = Me$) do not react with carbenoids



SCHEME

on either their sulphur atoms, or on their double-bonds. Instead attack on the thiazoline nitrogen dominates to give intermediates that can be trapped by intermolecular cycloaddition, at least for the carbenoid derived from ethyl diazoacetate and $Cu(acac)_2$.

EXPERIMENTAL

M.p.s were recorded on a Buchi 510 apparatus. I.r. spectra were recorded on Perkin-Elmer 257 and 297 spectrophotometers, and n.m.r. spectra on Perkin-Elmer R24 and Bruker WH 300 spectrometers. Chemical ionization mass spectra were recorded on a VG-micromass ZAB-IF spectrometer.

Short column chromatography was used for preparative purposes using Hopkin and Williams silica gel for t.l.c. (20–50 mesh, MFC without binder). All solvents were dried and distilled before use. Ether refers to diethyl ether and light petroleum refers to the fraction boiling at 30—40 °C

Methyl (2R)-2-[(1R, 3S, 4R, 5S, 6S, 8R)-3-*Benzyl*-4,5,6-*trisethoxycarbonyl*-9-*oxo*-7,10-*diaza*-2-*thiatricyclo*[6.2.0.0^{3,7}]-*decan*-10-*yl*]-3-*methylbut*-3-*enoate* (3).—Ethyl diazoacetate (0.5 g) was added dropwise to a solution of non-conjugated thiazoloazetidinone (1; $R^1 = PhCH_2$; $R^2 = Me$) (329 mg) and $Cu(acac)_2$ (24 mg) in anhydrous dichloromethane (5 ml) under nitrogen. The solution was warmed gently (*ca.* 30 °C) until effervescence subsided, and was stirred at 20 °C for 16 h. The reaction mixture was then diluted with dichloromethane, washed with water, dried ($MgSO_4$), and concentrated under reduced pressure to give an oil (791 mg) which was chromatographed repeatedly on silica (eluted with ether–light petroleum). The first fractions off the column contained diethyl maleate and diethyl fumarate.

The next product eluted was the adduct (3) (202 mg) which was crystallised from ether–light petroleum to give *methyl* (2R)-2-[(1R, 3S, 4R, 5S, 6S, 8R)-3-*benzyl*-4,5,6-*trisethoxycarbonyl*-9-*oxo*-7,10-*diaza*-2-*thiatricyclo*[6.2.0.0^{3,7}]*decan*-10-*yl*]-3-*methylbut*-3-*enoate* (3), m.p. 99—100 °C; $[\alpha]_D$ −229° (EtOH); $\nu_{max.}$ ($CHCl_3$) 1 750br, 1 375, 1 200br, and 1 020 cm^{-1}; δ($CDCl_3$) 1.17, 1.33, and 1.37 (each 3 H, t, *J* 7.5 Hz, CH_2CH_3), 1.95 (3 H, s, =CCH_3), 3.42 and 3.44 (each 1 H, d, *J* 13 Hz, CH_2Ph), 3.70 (1 H, d, *J* 10 Hz, $CHCO_2Et$), 3.78 (1 H, m, $CHCO_2Et$), 3.79 (3 H, s, CO_2Me), 3.96 (1 H, d, *J* 8 Hz, $CHCO_2Et$), 3.95—4.1 (2 H, m, CH_2CH_3), 4.2—4.4 (4 H, m, 2 × CH_2CH_3), 4.85 (1 H, s, $NCHCO_2Me$), 5.08 and 5.19 (each 1 H, br s, vinylic H), 5.34 and 6.01 (each 1 H, d, *J* 4 Hz, NCHCHS), 7.2—7.4 (3 H, m, aromatic H), and 7.52 (2 H, m, aromatic H); *m/e* 589 (M^+ + 1) and 497 (M^+ − $PhCH_2$; base peak) (Found: C, 59.0; H, 6.4; N, 4.8; S, 5.5. $C_{29}H_{36}N_2O_9S$ requires C, 59.17; H, 6.16; N, 4.76; S, 5.45%). Finally a small amount of the unchanged thiazoloazetidinone (1) (78 mg) was obtained.

Methyl 2-[(1R, 3S, 4R, 5S, 6S, 8R)-3-*Benzyl*-4,5,6-*tris-ethoxycarbonyl*-9-*oxo*-7,10-*diaza*-2-*thiatricyclo*[6.2.0.0^{3,7}]-*decan*-10-*yl*]-3-*methylbut*-2-*enoate* (5).—Using the procedure described above, the conjugated thiazoloazetidinone (2; R^1 = $PhCH_2$, R^2 = Me) (329 mg) and ethyl diazoacetate (0.5 g) in dichloromethane (5 ml) containing $Cu(acac)_2$ (24 mg) gave an oil (742 mg) which was chromatographed on silica (22 g), with ether–light petroleum as eluant to give *methyl* 2-[(1R, 3S, 4R, 5S, 6S, 8R)-3-*benzyl*-4,5,6-*trisethoxycarbonyl*-9-*oxo*-7,10-*diaza*-2-*thiatricyclo*[6.2.0.0^{3,7}]*decan*-10-*yl*]-3-*methylbut*-2-*enoate* (5) (169 mg), m.p. 110—111 °C; $[\alpha]_D$ −185° (EtOH); $\nu_{max.}$ 1 740br, 1 385, 1 370, 1 220, and 1 020 cm^{-1}; δ($CDCl_3$) 1.14, 1.32, and 1.35 (each 3 H, t, *J* 7.5 Hz, 3 × CH_2CH_3), 2.06 and 2.23 (each 3 H, s, =CMe_2), 3.48 and 3.59 (each 1 H, d, *J* 15 Hz, CH_2Ph), 3.73 (2 H, m, 2 × $CHCO_2Et$), 3.78 (3 H, s, CO_2Me), 3.9 (1 H, dd, *J* 3,7 Hz, $CHCO_2Et$), 4.00 (2 H, m, CH_2CH_3), 4.2—4.3 (4 H, m, 2 × CH_2CH_3), 5.38 and 5.85 (each 1 H, d, *J* 4 Hz, NCH·CHS), 7.2—7.4 (3 H, m, aromatic H), and 7.5 (2 H, m, aromatic H); *m/e* 589 (M^+ + 1) and 497 (base peak, M^+ − $PhCH_2$) (Found: C, 59.25; H, 6.25; N, 4.85; S, 5.1%).

Methyl (2R)-2-[(1R, 3S, 4R, 5S, 6S, 8R)-3-*Benzyl*-4,5-*bismethoxycarbonyl*-6-*ethoxycarbonyl*-9-*oxo*-7,10-*diaza*-2-*thiatricyclo*[6.2.0.0^{3,7}]*decan*-10-yl]-3-*methylbut*-3-*enoate* (4).—Ethyl diazoacetate (0.5 ml) was added dropwise to a solution of non-conjugated thiazoloazetidinone (1) (310 mg), dimethyl fumarate (271 mg), and $Cu(acac)_2$ (47 mg) in anhydrous dichloromethane (5 ml) under nitrogen. Effervescence was seen on gentle warming, and the reaction mixture was stirred for 16 h at 20 °C. Work-up as usual gave a brown oil (0.96 g) which was chromatographed on silica to give *methyl* (2R)-2-[(1R, 3S, 4R, 5S, 6S, 8R)-3-*benzyl*-4,5-*bismethoxycarbonyl*-6-*ethoxycarbonyl*-9-*oxo*-7,10-*diaza*-2-*thiatricyclo*[6.2.0.0^{3,7}]*decan*-10-*yl*]-3-*methylbut*-3-*enoate* (4) (148 mg), crystallized from ether–light petroleum, m.p. 147—148 °C; $[\alpha]_D$ −125° (EtOH); $\nu_{max.}$ 1 740, 1 440, 1 380, 1 336, 1 220, 1 178, 1 010, and 912 cm^{-1}; δ($CDCl_3$) 1.3 (3 H, t, *J* 7.5 Hz, CH_2CH_3), 1.94 (3 H, s, =CMe), 3.38 (2 H, s, $PhCH_2$), 3.51 (3 H, s, CO_2Me), 3.71 (1 H, d, *J* 10 Hz, $CHCO_2Me$), 3.76 and 3.81 (each 3 H, s, CO_2Me), 3.78 (1 H, m, $CHCO_2Me$), 4.01 (1 H, d, *J* 8 Hz, $CHCO_2Et$), 4.1—4.35 (2 H, m, CH_2CH_3), 4.82 (1 H, s, $NCHCO_2Me$), 5.06 and 5.17 (each 1 H, d, *J* <1 Hz, vinylic H), 5.36 and 5.99 (each 1 H, d, *J* 4 Hz, NCHCHS), 7.18—7.35 (3 H, m, aromatic H), and 7.48 (2 H, m, aromatic H); *m/e* 561 (M^+ + 1) and 469 (base peak; M^+ − $PhCH_2$) (Found: C, 57.75; H, 5.8; N, 5.15; S, 5.75. $C_{27}H_{32}N_2O_9S$ requires C, 57.85; H, 5.75; N, 5.00; S, 5.72%).

Methyl 2-[(1R, 3S, 4R, 5S, 6S, 8R)-3-*Benzyl*-4,5-*bis-methoxycarbonyl*-6-*ethoxycarbonyl*-9-*oxo*-7,10-*diaza*-2-*thia-tricyclo*[6.2.0.0^{3,7}]*decan*-10-yl]-3-*methylbut*-2-*enoate* (6).—Using the procedure described above, the conjugated thiazoloazetidinone (2; R^1 = $PhCH_2$, R^2 = Me) (221 mg), dimethyl fumarate (195 mg), and ethyl diazoacetate (220 mg), in dichloromethane (3 ml), in the presence of $Cu(acac)_2$ (35 mg), gave an oil (790 mg) which on chromatography gave the trisethoxycarbonyl adduct (5) (21 mg) together with unchanged thiazoloazetidinone (2; R^1 = $PhCH_2$, R^2 = Me) (48 mg), and *methyl* 2-[(1R, 3S, 4R, 5S, 6S, 8R)-3-*benzyl*-4,5-*bismethoxycarbonyl*-6-*ethoxycarbonyl*-9-*oxo*-7,10-*diaza*-2-*thiatricyclo*[6.2.0.0^{3,7}]*decan*-10-*yl*]-3-*methylbut*-2-*enoate* (6) (82 mg), recrystallised from ether–light petroleum, m.p. 138—139 °C; $[\alpha]_D$ −115° (EtOH); $\nu_{max.}$ ($CHCl_3$) 1 740br, 1 438, 1 370, 1 215 br, and 1 020 cm^{-1}; δ($CDCl_3$) 1.31 (3 H, t, *J* 7.5 Hz, CH_2CH_3), 2.05 and 2.22 (each 3 H, s, =CMe_2), 3.44 (1 H, d, *J* 13 Hz, benzylic H), 3.52 (3 H, s, CO_2Me), 3.61 (1 H, d, *J* 13 Hz, benzylic H), 3.75 (2 H, m, 2 × $CHCO_2R$), 3.77 and 3.81 (each 3 H, s, CO_2Me), 4.00 (1 H, dd, *J* 3, 7 Hz, $CHCO_2Me$), 4.15—4.4 (2 H, m, CH_2CH_3), 5.41 and 5.86 (each 1 H, d, *J* 4 Hz, NCHCHS), 7.24—7.4 (3 H, m, aromatic H), and 7.5 (2 H, m, aromatic H); *m/e* 561 (M^+ + 1) and 469 (base peak, M^+ − $PhCH_2$) (Found: C, 57.6; H, 5.7; N, 5.05; S, 5.4%).

Isomerization of Non-conjugated Adduct (3).—Adduct (3) (70 mg), and triethylamine (30 mg) in chloroform were stirred at 20 °C for 16 h after which time no starting material could be seen by t.l.c. Column chromatography on silica gave the conjugated adduct (5) (67 mg) exclusively, no other product could be detected.

X-*Ray Structure Determination of Compound* (6).—Crystals of (6), $C_{27}H_{32}N_2O_9S$, *M* = 560.63, are triclinic *a* = 7.796(1), *b* = 9.815(2), *c* = 10.746(2) Å, α = 115.64(2), β = 97.70(2), γ = 101.37(1)°, *U* = 704 Å^3, space group *P*1, *Z* = 1, D_c = 1.33 g cm^{-3}.

Data were measured using monochromatised Cu-K_α radiation (graphite monochromator) on a Nicolet R3m diffractometer. A total of 2 068 independent reflections were measured ($0 \leqslant 58°$) using the omega-scan measuring routine, and of these 8 had $|F_o| < 3\sigma(|F_o|)$ and were classed as unobserved. The net counts of two reflections, the 2 T 1 and the 2 T 2, measured as references every 100 reflections did not alter significantly during the data collection (*ca.* 14 h) indicating that no deterioration of the crystal had occurred. The data were brought to a uniform arbitrary scale by use of these reflections and Lorentz and polarisation corrections were applied.

The structure was solved by direct methods, though not without some difficulty. Initial attempts at automatic solution were unsuccessful. However, a starting set comprising the 4 principal contributors to the list of strongest negative quartets together with a further 10 automatically selected origin and magic integer terms led to a tangent refinement (a total of 1 830 permutations) that gave encouraging figures of merit. 4 Cycles of weighted difference *E*-map recycling for the best solution gave *ca.* 80% of the molecule. The remaining atoms were then found in a conventional difference electron-density map.

The non-hydrogen atoms were refined anisotropically. The hydrogen atoms, with the exception of those of the methyl groups which were refined as rigid bodies, were placed at calculated positions and allowed to ride on their

parent carbons. Refinement was terminated at $R = 0.039$. The absolute configuration was confirmed by refinement of a single 'free variable' η which multiplies all F''. This variable refined to a value of $+1.01(4)$ indicating that the co-ordinate set was of the correct chirality.[12]

Computations were carried out on an Eclipse S 140 computer using the SHELXTL progress system.

TABLE 1

Fractional co-ordinates ($\times 10^4$) for the non-hydrogen atoms with estimated standard deviations in parentheses

Atom	x	y	z
S(1)	2 621	11 336	12 954
C(2)	4 095(4)	10 917(3)	11 645(3)
N(3)	5 113(3)	9 935(3)	11 897(3)
C(4)	4 115(4)	8 927(4)	12 364(3)
C(5)	2 659(4)	9 595(4)	13 106(3)
N(6)	1 312(4)	8 117(3)	12 031(3)
C(7)	2 513(4)	7 511(4)	11 296(4)
O(7)	2 322(3)	6 287(3)	10 249(3)
C(8)	5 547(4)	12 435(3)	11 940(3)
C(9)	7 384(4)	12 155(4)	12 282(3)
C(10)	6 999(4)	10 801(4)	12 659(3)
C(11)	2 844(4)	10 101(4)	10 134(3)
C(12)	3 776(4)	9 797(4)	8 944(3)
C(13)	4 011(5)	10 822(4)	8 365(4)
C(14)	4 861(6)	10 566(5)	7 276(4)
C(15)	5 515(6)	9 303(6)	6 758(4)
C(16)	5 295(6)	8 255(6)	7 296(4)
C(17)	4 417(5)	8 502(4)	8 391(4)
C(18)	5 296(5)	13 906(4)	13 064(3)
O(18)	6 285(4)	14 746(3)	14 230(3)
O(19)	3 801(4)	14 168(3)	12 557(3)
C(20)	3 252(7)	15 455(5)	13 519(5)
C(21)	8 298(4)	11 797(4)	11 069(3)
O(21)	8 617(4)	10 602(3)	10 386(3)
O(22)	8 686(4)	13 063(3)	10 859(3)
C(23)	9 520(6)	12 908(5)	9 695(4)
C(24)	7 460(5)	11 461(4)	14 270(3)
O(24)	6 445(4)	11 477(4)	14 994(3)
O(25)	9 244(4)	12 022(4)	14 757(3)
C(26)	9 967(7)	12 802(8)	16 313(5)
C(27)	11 779(10)	13 537(12)	16 675(7)
C(28)	−535(4)	7 491(4)	11 932(4)
C(29)	−947(4)	7 672(4)	13 307(4)
O(29)	379(3)	7 574(3)	14 137(3)
O(30)	−2 300(4)	7 935(4)	13 650(3)
C(31)	125(6)	7 779(6)	15 503(4)
C(32)	−1 800(4)	6 725(4)	10 693(4)
C(33)	−1 443(5)	6 701(4)	9 349(4)
C(34)	−3 676(5)	5 798(5)	10 530(5)

TABLE 2

Bond lengths with e.s.d.'s in parentheses

S(1)–C(2)	1.894(3)	S(1)–C(5)	1.791(4)
C(2)–N(3)	1.449(5)	C(2)–C(8)	1.559(4)
C(2)–C(11)	1.540(4)	N(3)–C(4)	1.438(5)
N(3)–C(10)	1.462(4)	C(4)–C(5)	1.561(5)
C(4)–C(7)	1.536(4)	C(5)–N(6)	1.471(3)
N(6)–C(7)	1.366(5)	N(6)–C(28)	1.420(4)
C(7)–O(7)	1.203(3)	C(8)–C(9)	1.538(5)
C(8)–C(18)	1.499(4)	C(9)–C(10)	1.536(6)
C(9)–C(21)	1.511(5)	C(10)–C(24)	1.522(5)
C(11)–C(12)	1.503(5)	C(12)–C(13)	1.389(6)
C(12)–C(17)	1.376(6)	C(13)–C(14)	1.374(6)
C(14)–C(15)	1.354(7)	C(15)–C(16)	1.375(9)
C(16)–C(17)	1.395(6)	C(18)–O(18)	1.200(4)
C(18)–O(19)	1.338(5)	O(19)–C(20)	1.431(6)
C(21)–O(21)	1.181(4)	C(21)–O(22)	1.342(5)
O(22)–C(23)	1.451(6)	C(24)–O(24)	1.179(5)
C(24)–O(25)	1.329(4)	O(25)–C(26)	1.473(5)
C(26)–C(27)	1.369(9)	C(28)–C(29)	1.496(6)
C(28)–C(32)	1.342(4)	C(29)–O(29)	1.320(5)
C(29)–O(30)	1.202(5)	O(29)–C(31)	1.439(6)
C(32)–C(33)	1.498(6)	C(32)–C(34)	1.505(6)

Table 1 lists the fractional atomic co-ordinates. Tables 2 and 3 give the bond lengths and valence angles respectively. The anisotropic thermal parameters, the structure factors, and the hydrogen co-ordinates and temperature factors have been treated as a Supplementary publication [SUP. No. 23339 (16 pp)].*

TABLE 3

Bond angles (°) with e.s.d.'s in parentheses

C(2)–S(1)–C(5)	92.3(2)	S(1)–C(2)–N(3)	106.5(2)
S(1)–C(2)–C(8)	112.3(2)	N(3)–C(2)–C(8)	105.1(2)
S(1)–C(2)–C(11)	107.6(2)	N(3)–C(2)–C(11)	113.1(2)
C(8)–C(2)–C(11)	112.1(3)	C(2)–N(3)–C(4)	112.0(3)
C(2)–N(3)–C(10)	112.7(2)	C(4)–N(3)–C(10)	118.5(3)
N(3)–C(4)–C(5)	112.9(3)	N(3)–C(4)–C(7)	119.5(3)
C(5)–C(4)–C(7)	85.1(2)	S(1)–C(5)–C(4)	107.6(3)
S(1)–C(5)–N(6)	116.9(3)	C(4)–C(5)–N(6)	87.4(2)
C(5)–N(6)–C(7)	95.1(2)	C(5)–N(6)–C(28)	131.2(3)
C(7)–N(6)–C(28)	133.3(2)	C(4)–C(7)–N(6)	92.3(2)
C(4)–C(7)–O(7)	135.9(3)	N(6)–C(7)–O(7)	131.7(3)
C(2)–C(8)–C(9)	105.8(3)	C(2)–C(8)–C(18)	112.6(3)
C(9)–C(8)–C(18)	114.6(2)	C(8)–C(9)–C(10)	105.7(3)
C(8)–C(9)–C(21)	112.6(3)	C(10)–C(9)–C(21)	112.5(3)
N(3)–C(10)–C(9)	103.6(3)	N(3)–C(10)–C(24)	116.8(3)
C(9)–C(10)–C(24)	110.0(2)	C(2)–C(11)–C(12)	115.7(3)
C(11)–C(12)–C(13)	120.7(3)	C(11)–C(12)–C(17)	121.4(4)
C(13)–C(12)–C(17)	118.0(4)	C(12)–C(13)–C(14)	121.6(4)
C(13)–C(14)–C(15)	119.9(5)	C(14)–C(15)–C(16)	120.2(5)
C(15)–C(16)–C(17)	120.0(5)	C(12)–C(17)–C(16)	120.3(5)
C(8)–C(18)–O(18)	126.0(4)	C(8)–C(18)–O(19)	109.3(2)
O(18)–C(18)–O(19)	124.7(3)	C(18)–O(19)–C(20)	117.5(3)
C(9)–C(21)–O(21)	126.7(4)	C(9)–C(21)–O(22)	109.0(3)
O(21)–C(21)–O(22)	124.2(4)	C(21)–O(22)–C(23)	116.5(3)
C(10)–C(24)–O(24)	127.3(3)	C(10)–C(24)–O(25)	108.4(3)
O(24)–C(24)–O(25)	124.3(3)	C(24)–O(25)–C(26)	116.9(3)
O(25)–C(16)–C(27)	110.6(5)	N(6)–C(28)–C(29)	114.8(3)
N(6)–C(28)–C(32)	122.7(4)	C(29)–C(28)–C(32)	122.4(3)
C(28)–C(29)–O(29)	112.4(3)	C(28)–C(29)–O(30)	124.3(4)
O(29)–C(29)–O(30)	123.2(4)	C(29)–O(29)–C(31)	116.4(3)
C(28)–C(32)–C(33)	122.5(3)	C(28)–C(32)–C(34)	123.0(4)
C(33)–C(32)–C(34)	114.5(3)		

* For details of the Supplementary publications scheme see Notice to Authors No. 7, *J. Chem. Soc., Perkin Trans. 1*, 1981, Index issue.

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