3,7-BIS(CARBOETHOXY)PERHYDRO-1,5,2,4,6,8-DITHIATETRAZOCINE 1,1,5,5-TETROXIDE. SYNTHESIS, STRUCTURE AND CHEMISTRY.

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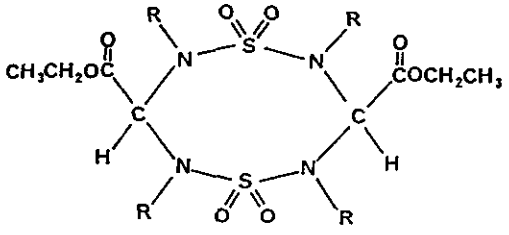
Abstract. - The synthesis and single-crystal X-ray crystallographic analysis of 3,7-bis(carboethoxy)perhydro-1,5,2,4,6,8,-dithiatetrazocine 1,1,5,5-tetroxide (1) and the corresponding permethylated derivative 2 is detailed. The use of 1 in electrophilic aromatic substitution transformations with benzene, toluene, and anisole is also described.

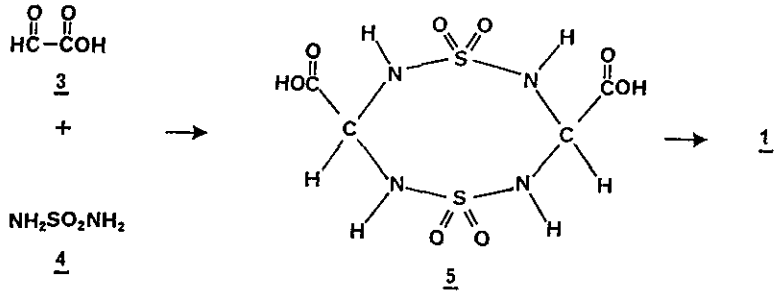
Few reports have appeared concerning perhydrodithiatetrazocines.[1-5] Little information is known about their structure and chemical reactivity. In this paper, we report the synthesis and X-ray crystallographic analysis of 3,7-bis(carboethoxy)perhydro-1,5,2,4,6,8-dithiatetrazocine 1,1,5,5-tetroxide (1) and the corresponding permethylated derivative 2, and the use of 1 in electrophilic aromatic substitution processes.



1 R = H
2 R = CH_3

Results and Discussion.

Synthesis of the title compound was patterned after previous procedures.[3,4] Treatment of glyoxylic acid (3) with sulfamide (4), followed by esterification with ethanol and sulfuric acid gave 1 in 29% overall yield.



3 + 4 → 5 → 1

The mass, infrared, ^1H and ^{13}C nmr spectral properties along with elemental analysis for 1 supported the proposed structural assignment. Mass spectrometry (CI mode) showed a molecular ion peak (P + I) at m/e 361.

The infrared spectrum showed prominent bands at 1730 cm^{-1} for the carboethoxy moiety and 1310 and 1160 cm^{-1} for the sulfamide group.[6] The ^1H nmr spectrum displayed a triplet (J = 9.5 Hz) at δ 5.25 and a doublet (J = 9.5 Hz) at δ 8.10 for the ring methine and sulfamide N-H protons, respectively. Significantly, only four signals were observed in the proton-decoupled ^{13}C nmr spectrum. The absence of additional peaks in the ^{13}C nmr spectrum strongly suggested that the reaction proceeded with the formation of a single geometric stereoisomer. Verification of this contention was secured from the single-crystal X-ray crystallographic study of 1. An ORTEP drawing of 1 (Figure 1) shows that the ring adopts a staggard conformation in the solid state, with the two carboethoxy groups occupying equatorial-like positions. The preferred ring conformation of 1 differed considerably from the structures reported for related compounds.[7,8] X-ray diffraction analysis showed that the eight-membered ring in both 3,7-diphenyl- and 3,7-bis (p-methoxyphenyl)- 1,5,2,4,6,8-diathiatetrazocine was planar,[7a] while in 3,7-bis(dimethylamino)- 1,5,2,4,6,8-dithiatetrazocine[7a] and the corresponding S-chloro salt[8] the ring was folded along an axis drawn through the sulfur atoms.

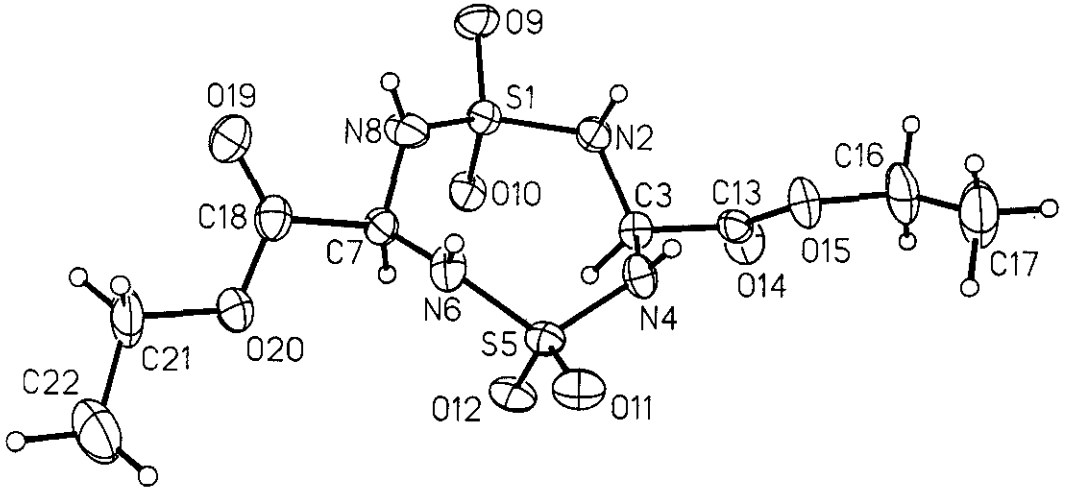
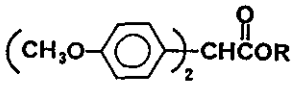


Figure 1. ORTEP drawing (30% probability ellipsoids) of 1. Selected bond lengths (in Å) and bond angles (in ° C) are: S(1)-O(9) 1.414 (3), S(1)-O(10) 1.431 (3), S(1)-N(2) 1.616 (3), N(2)-H(2) 0.795 (43), N(2)-C(3) 1.452 (5), C(3)-H(3) 1.050, N(4)-C(3) 1.452 (5), S(5)-N(4) 1.608 (4), S(5)-O(11) 1.424 (3), S(5)-O(12) 1.429 (3), S(5)-N(6) 1.603 (4), N(6)-H(6) 0.767 (41), N(6)-C(7) 1.450 (5), N(8)-C(7) 1.449 (5), C(7)-H(7) 1.050, S(1)-N(8) 1.604 (4); O(10)-S(1)-O(9) 121.9 (2), N(2)-S(1)-O(9) 106.8 (2), N(2)-S(1)-O(10) 104.4 (2), C(3)-N(2)-S(1) 121.9 (3), C(3)-N(4)-S(5) 121.3(3).

Evidence that the overall reaction proceeded via the intermediacy of the corresponding dicarboxylic acid 5 was obtained by inspection of the ^{13}C nmr spectrum of the crude product mixture prior to esterification. Two prominent signals were observed at 60.60 and 167.78 ppm consistent with 5. Furthermore, treatment of crude 5 with excess anisole and methanesulfonic acid led to a moderate yield of bis(4-methoxyphenyl)acetic acid (6).[9]



6 R = H

7 R = CH_2CH_3

Dithiatetrazocine 1 was readily converted to the tetramethyl derivative 2 upon treatment with methyl iodide and base. Analysis of the single-crystal X-ray structure for 2 indicated that the ring contained C_2-symmetry and that the two sets of transannular N-methyl groups (i.e., N2, N6 versus N4, N8) occupied different orientations (Figure 2). The corresponding 300 MHz ^1H nmr spectrum of 2 in acetone-d_6 at -75 °C, however, showed only a sharp singlet for the N-methyl protons at δ 3.12. The equivalence of the two sets of methyl protons suggests that the ring is conformationally mobile at this temperature. Comparison of the crystal structures of 1 and 2 indicated that the solid state conformation of both eight-membered rings were nearly identical despite the fact that 1 undergoes extensive intermolecular hydrogen-bonding while 2 cannot.

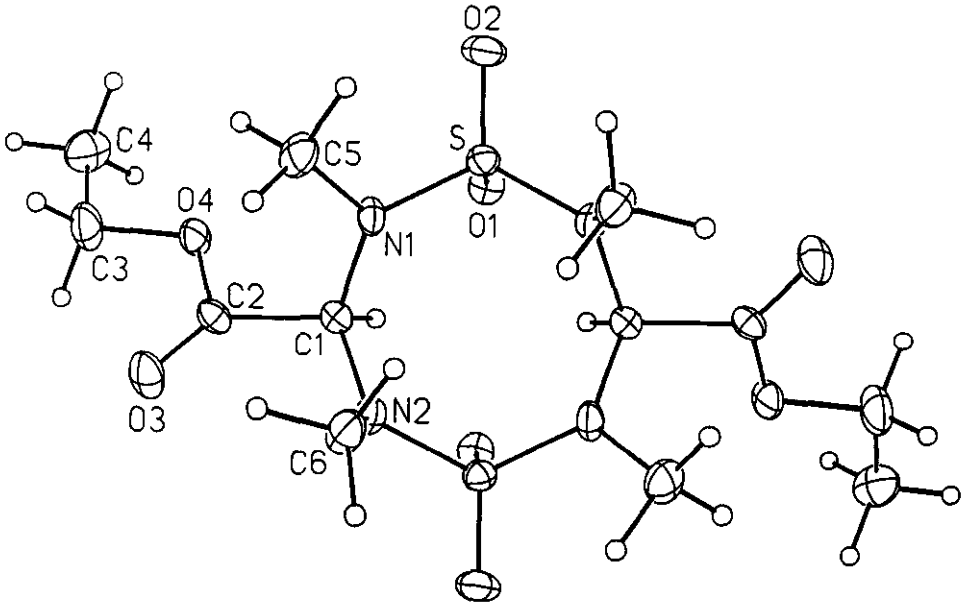
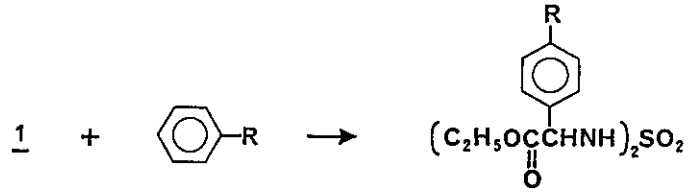


Figure 2. ORTEP drawing (30% probability ellipsoids) of 2. Two independent molecules were observed (only one shown). The only major difference between the geometries of the two molecules is the orientation of the side-chain terminal ethyl groups. Selected bond lengths (in Å) and bond angles (in ° C) are: S-O (1) 1.435 (7), S-O(2) 1.402 (7), S-N(1) 1.617 (8), N(1)-C(5) 1.503 (12), N(1)-C(1) 1.447 (11), C(1)-C(2) 1.524 (13), C(1)-H(1) 1.050, N(2)-C(1) 1.459 (11), N(2)-C(6) 1.568 (13); O(2)-S-O(1) 120.5 (5), N(1)-S-O(1) 106.7 (5), N(1)-S-O(2) 107.4 (5), C(1)-N(1)-S 119.6 (7), C(5)-N(1)-S 119.1 (7), C(5)-N(1)-C(1) 121.2 (8), C(6)-N(2)-C(1) 118.4(8), C(1)-N(2)-S" 118.4 (7), C(6)-N(2)-S" 114.7 (7), N(2)-C(1)-N(1) 114.5 (8).

The potential use of 1 as an amidoalkylating reagent has been examined. Treatment of 1 with either benzene (8) or toluene (9) and methanesulfonic acid gave 11 and 12, respectively. In both cases, the product mixture consisted of a 1:1 diastereomeric mixture of the dl-racemate and meso adducts which were separable by flash chromatography. Use of anisole in this procedure gave ethyl bis(4-methoxyphenyl)acetate (7).[9] Apparently, in the case of anisole the initially generated adduct 13 is sufficiently reactive to undergo a second electrophilic aromatic substitution process.



8 R = H 11 R = H

9 R = CH_3 12 R = CH_3

10 R = OCH_3 13 R = OCH_3

EXPERIMENTAL SECTION.

General Methods. Infrared spectra (ir) were run on a Perkin-Elmer 283 spectrometer and calibrated against the 1601 cm^{-1} band of polystyrene. Proton (^1H nmr) and carbon (^{13}C nmr) nuclear magnetic resonance spectra were taken on a Nicolet NT-300 and General Electric QE-300 nmr instruments. Low resolution mass spectral data (ms) were obtained at an ionizing voltage of 70 eV on a Bell and Howell 21-491 mass spectrometer at the University of Texas-Austin. High resolution mass spectra were performed on a CEC 21-110B double focusing magnetic-sector spectrometer at the University of Texas-Austin by Dr. John Chinn. Elemental analysis were obtained from Spang Microanalytical Laboratory, Eagle Harbor, Michigan. All glassware was dried before use. The solvents and reactants were of the best commercial grade available and were used without further purification.

Preparation of 3,7-Bis(carboethoxy)perhydro-1,5,2,4,6,8-dithiatetrazocine 1,1,5,5-Tetroxide (1).

A solution of glyoxylic acid (3) (50 wt. % solution in water, 0.74 g, 5 mmol) and sulfamide (4) (0.48 g, 5 mmol) was heated with stirring at 50°C (5h) and then concentrated under vacuum. The residue was dissolved in absolute ethanol (25 mL), cooled to 20°C, and then concentrated sulfuric acid (0.2 mL) was added. The solution was stirred at room temperature (3 d), and then evaporated to dryness. The residue was triturated with diethyl ether-hexane (1:1) and the remaining white solid was recrystallized from ethanol to afford 0.53 g (29%) of 1 (R_f 0.18, 25% acetone-chloroform): mp 203-205 °C (dec.); ir (KBr) 3250, 1730, 1310, 1160 cm^{-1}; ^1H nmr (Me_2SO-d_6) δ 1.23 (t, J = 7 Hz, 6H), 4.17 (q, J = 7 Hz, 4H), 5.25 (t, J = 9.5 Hz, 2H), 8.10 (d, J = 9.5 Hz, 4H, D_2O exchangeable); ^{13}C nmr (Me_2SO-d_6) 13.89, 62.04, 64.52, 165.88 ppm; ms (CI), 361 (P+1).

Anal. Calcd for $C_8H_{16}N_4O_8S_2$: C, 26.67; H, 4.48; N, 15.55; S, 17.80. Found: C, 26.61; H, 4.61; N, 15.48; S, 17.75.

Preparation of Bis(4-methoxyphenyl)acetic Acid (6).

A solution of glyoxylic acid (3) (50% wt. solution in water, 0.34 g, 2.5 mL) and sulfamide (4) (0.24 g, 2.5 mmol) was heated with stirring at 50 °C (5 h) and then concentrated to dryness. To the remaining residue, anisole (10) (3 mL) and methanesulfonic acid (0.5 mL, 7.7 mmol) was added and the mixture was stirred at room temperature (2 d). Diethyl ether (50 mL) was added and then the ether solution was washed with water (3 X 50 mL), dried (Na_2SO_4), and evaporated in vacuo. The yellow solid was dissolved in aqueous 1% sodium hydroxide solution (20 mL) and the solution was acidified with aqueous hydrochloric acid solution. The light brown solid was filtered and dried to give 0.36 g (53%) of 6 (R_f 0.67, methanol: methylene chloride: acetone = 1:3:5); mp 109-111 °C (lit.[9b] mp 111-112°C); ir (KBr) 3550-2500 (br), 2040, 1880, 1695, 1600 cm^{-1}; ^1H nmr ($CDCl_3$) δ 3.76 (s, 6H), 4.93 (s, 1H), 6.84 (d, J = 8 Hz, 4H), 7.22 (d, J = 8 Hz, 4H), 10.20 (br s, 1H); ^{13}C nmr ($CDCl_3$) 55.21, 55.33, 113.98, 129.61, 130.35, 158.79, 179.15 ppm.

Preparation of 3,7-Bis(carboethoxy)-2,4,6,8-tetramethylperhydro-1,5,2,4,6,8- dithiatetrazocine 1,1,5,5-Tetroxide (2).

A mixture of diester 1 (0.36 g, 1 mmol), methyl iodide (1.2 mL, 8 mmol), anhydrous potassium carbonate (1.31 g, 9.5 mmol) and acetone (30 mmol) was stirred at room temperature (3d). The solid was filtered, and the filtrate was concentrated in vacuo. The solid residue was recrystallized from acetone-hexane to give 0.12 g (24%) of 2 (R_f 0.85, 25% acetone-chloroform); mp 223-225 °C (dec.); ir (KBr) 1745, 1360, 1170 cm^{-1}; ^1H nmr (Me_2SO-d_6) δ 1.26 (t, J = 7 Hz, 6H), 3.12 (s, 12H), 4.25 (q, J = 7 Hz, 4H), 6.33 (s, 2H); ^{13}C nmr (Me_2SO-d_6) 13.78, 34.45, 62.79, 71.07, 164.15 ppm; ms, m/z (relative intensity) 417 (8), 343 (66), 250 (100), 209 (33), 208 (28), 135 (28), 116 (62), 115 (65); mol wt 417.1120 (Calcd for $C_{12}H_{25}N_4O_8S_2$ 417.1114, M + 1).

Preparation of N,N'-Bis[(a-carboethoxy)benzyl]sulfamide (11).

A mixture of 1 (0.45 g, 1.25 mmol), benzene (8) (5 mL) and methanesulfonic acid (0.3 mL, 4.62 mmol) was stirred at room temperature (3 d). Diethyl ether (50 mL) was added to the reaction mixture, and the ether solution was washed with aqueous 5% sodium bicarbonate (3 X 50 mL), dried (Na_2SO_4), and concentrated in vacuo to give 0.32 g (61%) of a 1:1 mixture consisting of the dl-racemate and meso stereoisomers 11 (R_f 0.75 and 0.70, 5% acetone-chloroform). The diastereomers were separated by flash column chromatography using 5% acetone-chloroform as the eluent. The initial compound isolated possessed the following properties: R_f 0.75 (5% acetone-chloroform); mp 215-217 °C; ir (KBr) 3250, 1735, 1335, 1155 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.12 (t, J = 7 Hz, 6H), 4.06 (q, J = 7 Hz, 4H), 4.98 (d, J = 7.5 Hz, 2H), 5.68 (d, J = 7.5 Hz, 2H), 7.32 (s, 10H); ^{13}C nmr ($CDCl_3$)13.73, 59.60, 62.05, 127.13, 128.50, 128.76, 135.82, 170.35 ppm.

Anal. Calcd for $C_{20}H_{24}N_2O_6S$: C, 57.13; H, 5.73; N, 6.66; S, 7.63. Found: C, 56.92; H, 5.78; N, 6.60; S, 7.69.

The following properties were observed for the second compound which eluted from the column: R_f 0.70 (5% acetone-chloroform); mp 205-207 °C; ir (KBr) 3250, 1735, 1335, 1155 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.19 (t, J = 7 Hz, 6H), 4.16 (t, J = 7 Hz, 4H), 5.00 (d, J = 7.5 Hz, 2H), 5.64 (d, J = 7.5 Hz, 2H), 7.22-7.32 (m, 10H); ^{13}C nmr ($CDCl_3$) 13.81, 59.97, 62.11, 127.20, 128.53, 128.82, 135.96, 170.69 ppm.

Anal. Calcd for $C_{20}H_{24}N_2O_6S$: C, 57.13; H, 5.73; N, 6.66; S, 7.63. Found: C, 56.96; H, 5.81; N, 6.68; S, 7.60.

Preparation of N, N'-Bis[(α-carboethoxy)-4-methylbenzyl]sulfamide (12).

Utilizing the procedure described for 11, 1 (0.45 g, 1.25 mmol), toluene (9) (5 mL), and methanesulfonic acid (0.3 mL, 4.62 mmol) were stirred at room temperature (3 d). After workup, a 1:1 stereoisomeric mixture of the dl-racemate and meso adducts of 12 was obtained in 64% yield (0.36 g) (R_f 0.85 and 0.80, 5% acetone-chloroform). The two sets of products were separated by flash chromatography using 5% acetone-chloroform as the eluent. The initial compound which was isolated from the column possessed the following properties: R_f 0.85 (5% acetone-chloroform); mp 225-227 °C (dec.); ir (KBr) 3240, 1730, 1335, 1155 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.14 (t, J = 7 Hz, 6H), 2.33 (s, 6H), 4.06 (q, J = 7 Hz, 4H), 4.92 (d, J = 7.5 Hz, 2H), 5.44 (d, J = 7.5 Hz, 2H), 7.15-7.21 (m, 8H); ^{13}C nmr ($CDCl_3$) 13.82, 21.10, 59.28. 62.12, 127.11, 129.57, 132.79, 138.80, 171.50 ppm.

Anal. Calcd for $C_{22}H_{28}N_2O_6S$: C, 58.91; H, 6.29; N, 6.25; S, 7.15. Found: C, 58.90; H, 6.35; N, 6.31; S, 7.10.

The second compound which was isolated had the following properties: R_f 0.80 (5% acetone-chloroform); mp 205-207 °C (dec.); ir (KBR) 3240, 1730, 1335, 1155 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.18 (t, J = 7Hz, 6H), 2.23 (s, 6H), 4.14 (q, J =7Hz, 4H), 4.96 (d, J = 7.5 Hz, 2H), 5.66 (d, J = 7.5 Hz, 2H), 7.07-7.13 (m, 8H); ^{13}C nmr ($CDCl_3$) 13.76, 20.90, 59.68, 61.94, 127.01, 129.37, 132.88, 138.24, 170.81 ppm.

Anal. Calcd for $C_{22}H_{28}N_2O_6S$: C, 58.91; H, 6.29; N, 6.25; S, 7.15. Found: C, 58.80; H, 6.30; N, 6.24; S, 7.18.

Preparation of Ethyl Bis(4-methoxyphenyl)acetate (7).

A mixture of 1 (0.63 g, 1.75 mmol), anisole (10) (4 mL) and methanesulfonic acid (0.4 mL, 4.62 mmol) was stirred at room temperature (24 h). Diethyl ether (50 mL) was added and then the ether solution was washed with aqueous 5% sodium bicarbonate (3 X 50 mL), dried (Na_2SO_4), and evaporated in vacuo. The residue was distilled under vacuum to give 0.54 g (52 %) of 7 (R_f 0.85, chloroform); bp 198-200 °C (2 torr) (lit.[9b] bp 130 °C (0.015 torr)); ir (KBr) 2060, 1890, 1740, 1600 cm^{-1}; ^1H nmr ($CDCl_3$) δ 1.24 (t, J = 7 Hz, 3H), 3.76 (s, 6H), 4.18 (q, J = 7 Hz, 2H), 4.90 (s, 1H), 6.83-7.23 (m, 8H); ^{13}C nmr ($CDCl_3$) 14.07, 55.14, 55.41, 60.97, 113.88, 129.47, 131.24, 158.64, 172.33 ppm; ms, m/z (relative intensity) 300 (10), 228 (20), 227 (100), 212 (6), 197 (2), 169 (4), 152 (4), 141 (6); mol wt 300.1364 (Calcd for $C_{18}H_{20}O_4$ 300.1362).

Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 72.06; H, 6.65.

Crystallographic Studies of Compounds 1 and 2.

Compound 1 was recrystallized from tetrahydrofuran-acetone as monoclinic crystals, $C_8H_{16}N_4O_8S_2$, space group $P2_1/c$, with a = 10.707 (3), b = 5.098 (1), c = 27.845 (8) Å, β = 97.34 (2)°, Z = 4, density = 1.59 $g\text{-}cm^{-3}$. Intensity measurements were made with Mo Kα radiation (λ = 0.71073 Å; graphite monochromator) on a Nicolet R3m/V automatic diffractometer in the ω mode to a limit of 45° 2θ. A total of 1382 unique reflections were corrected for Lorentz and polarization effects. The structure solution was obtained from TREF using the

SHELXTL PLUS direct methods, yielding coordinates for most of the non-hydrogen atoms in the asymmetric unit, which consists of one complete molecule. Hydrogens were entered in ideal calculated postions. Only the amino hydrogens were allowed to refine independently. A single variable isotropic thermal parameter was assigned to all the non-methyl hydrogen atoms, and a single non-variable one to all the methyl hydrogens. Compound 2 was recrystallized from acetone as monoclinic crystals, $C_{12}H_{24}N_4O_8S_2$, space group C2/c, with a = 19.261 (4), b = 12.301 (3), c = 17.268 (3) Å, β = 112.56 (1)°, Z = 8, density = 1.46 g-cm^{-3}. Intensity measurements were made with Mo Kα radiation (λ = 0.71073 Å; graphite monochromator) on a Nicolet R3m/V automatic difractometer in the ω mode to a limit of 45° 2 θ. A total of 1400 unique reflections were corrected for Lorentz and polarization effects. The structure was solved by use of the SHELXTL Patterson interpretation program, which revealed the positions of the two independent sulfur atoms in the asymmetric unit, which consists of two half-molecules situated about separate two-fold axes. Hydrogens were added at ideal calculated positions and constrained to riding motion. The methyl groups (excluding those in the terminal ethyl moieties) were treated as rigid groups, allowing free pivoting about the central carbons. Non-variable isotropic thermal parameters were assigned to all of the hydrogens, based on the thermal motion of their attached atoms. For compound 1 after all shift/esd ratios were less than 0.1, convergence was reached at R = 0.036 (R_w = 0.032). Correspondingly, after all shift/esd ratios were less than 0.4 for compound 2, convergence was reached at R = 0.069 (R_w = 0.057). No unusually high correlations were noted between any of the variables in the last cycle of full-matrix least squares refinement, and the final difference density map showed no peak greater than 0.20 e/Å^3 for 1 and 0.5 e/Å^3 for 2. All calculations were made using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs. Table 1 lists the atomic coordinates and equivalent isotropic displacement parameters for compounds 1 and 2.

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Table 1. Atomic Coordinates (X 10^4) and equivalent isotropic displacement parameters ($Å^2$ X 10^3) for compounds 1 and 2.

1

	x	y	z
S(1)	-2950(1)	3108(2)	1261(1)
S(5)	118(1)	2350(2)	631(1)
O(9)	-4041(3)	4419(6)	1373(1)
O(10)	-2642(3)	506(5)	1430(1)
O(11)	1029(2)	3229(5)	337(1)
O(12)	250(3)	-114(5)	877(1)
O(14)	-3708(3)	-2187(6)	57(1)
O(15)	-3190(3)	1273(6)	-377(1)
O(19)	-79(3)	7660(6)	2057(1)
O(20)	1417(3)	4684(6)	1990(1)
N(2)	-3076(3)	2883(7)	678(1)
N(4)	-1188(3)	2190(7)	277(1)
N(6)	90(4)	4502(6)	1050(1)
N(8)	-1782(4)	4925(7)	1469(2)
C(3)	-2310(4)	1074(8)	438(1)
C(7)	-479(4)	4116(8)	1490(2)
C(13)	-3156(4)	-171(9)	15(2)
C(16)	-3987(5)	324(11)	-810(2)
C(17)	-3486(5)	1240(13)	-1235(2)
C(18)	289(5)	5724(9)	1887(2)
C(21)	2270(5)	6035(11)	2357(2)
C(22)	3469(5)	4492(13)	2429(2)

2

	x	y	z
S	3965(1)	914(3)	1667(2)
O(1)	4097(4)	-236(6)	1742(4)
O(2)	3274(4)	1327(7)	1112(4)
O(3)	4628(5)	1131(7)	4700(5)
O(4)	3775(4)	92(6)	3757(4)
N(1)	4093(5)	1356(7)	2594(5)
N(2)	5386(4)	1384(7)	3628(5)
C(1)	4654(5)	848(8)	3321(6)
C(2)	4367(6)	754(9)	4026(7)
C(3)	3432(8)	-118(12)	4357(8)
C(4)	2852(7)	-926(11)	3993(8)
C(5)	3588(7)	2234(10)	2685(7)
C(6)	5414(7)	2645(10)	3773(8)
S'	3961(1)	4072(3)	7436(2)
O(1')	4088(4)	5226(6)	7472(4)
O(2')	3258(4)	3647(7)	7383(4)
O(3')	4665(4)	3886(6)	4997(4)
O(4')	3787(4)	4906(6)	5197(4)
N(1')	4098(5)	3632(7)	6621(5)
N(2')	5401(5)	3594(7)	6713(5)
C(1')	4660(5)	4138(8)	6390(6)
C(2')	4383(6)	4263(8)	5439(6)
C(3')	3466(7)	5134(11)	4309(7)
C(4')	2890(7)	4311(10)	3838(8)
C(5')	3605(7)	2737(10)	6097(7)
C(6')	5414(7)	2323(10)	6578(8)

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