solution was treated with sodium borohydride (12 g) added in small portions with cooling. After stirring for 18 h at room temperature, the reaction mixture was acidified with HCl and evaporated to dryness. The residue was made strongly basic with KOH and extracted with ether. Distillation [51–53 °C (0.15 mm)] of the residue obtained on evaporation of the dried (K_2CO_3) extract afforded the pyrrolidine **5** as a colorless oil (8.2 g, 59%): n^{25}_D 1.5551; IR (neat) ν_{max} 2760 (NMe), 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.70–6.87 (m, 4 H, aromatic), 3.70–3.10 (m, 2 H), 2.73–1.30 (complex multiplet, 8 H), with overlapping at δ 2.23 (NMe). It afforded a picrate, yellow needles from ethanol, mp 129.5–131 °C.

Anal. Calcd for $C_{17}H_{17}BrN_4O_7$: C, 43.51; H, 3.65; Br, 17.03; N, 11.94. Found: C, 43.77; H, 3.76; Br, 16.91; N, 12.17.

Dihydroshihunine (6). A solution of **5** (2.22 g) in dry THF (40 mL) was treated at −78 °C in a N_2 atmosphere over 30 min with 9 mL of *n*-butyllithium (2.3 M solution in hexane). After stirring for an additional 30 min the solution was saturated with dry CO_2 gas and allowed to warm to room temperature. The reaction mixture was then added to 5% HCl, concentrated, washed with ether, made strongly basic with KOH, and again extracted with ether. The aqueous solution was then acidified with HCl and chromatographed on a column of ion-exchange resin (BioRad, AG-50 W-X4, H^+ form). The column was washed with water, and then dihydroshihunine (1.38 g, 67%) eluted with 3 N ammonium hydroxide. Sublimation [130 °C (10^{-4} mm)] and crystallization from ethanol–ethyl acetate afforded colorless prisms, mp 184–194 °C (lit.[11] mp 190–201 °C) identical (mixed melting point, IR, NMR, MS) with an authentic specimen obtained by the hydrogenation of shihunine.

Oxidation of Dihydroshihunine to Shihunine. (a) With *N*-Bromosuccinimide. Dihydroshihunine (221 mg) was stirred for 18 h with *N*-bromosuccinimide (237 mg) in 5% aqueous $NaHCO_3$ (10 mL). Continuous extraction of the reaction mixture with CH_2Cl_2 afforded a brown gum (144 mg) which was subject to preparative TLC on alumina PF 254 (Merck) developing with a mixture of chloroform, methanol, and concentrated NH_3 (50:5:1). Shihunine (11 mg, 5%), R_f 0.43, and dihydroshihunine (62 mg, 28%), R_f 0.67, were obtained.

(b) With Mercuric Acetate. A solution of dihydroshihunine (158 mg) in 5% acetic acid (5 mL) containing mercuric acetate (1.0 g) was heated in a N_2 atmosphere for 2.5 h at 90–95 °C. The precipitated mercurous acetate (290 mg, 75%) which began to form almost immediately was removed by centrifuging. The supernatant solution was saturated with H_2S, again centrifuged, and then evaporated to dryness. The residue after TLC, as before, yielded shihunine (9 mg, 6%) and dihydroshihunine (33 mg, 21%).

Attempted oxidation of dihydroshihunine with bromine in CH_2Cl_2[7] failed to yield any shihunine.

One-Step Synthesis of Shihunine. A solution of *o*-bromobenzoic acid (2.50 g) in 50 mL of dry THF (distilled from $LiAlH_4$) was cooled to −100 °C using a bath of liquid N_2 and ethanol. The reaction mixture was maintained at −100 °C in a N_2 atmosphere while 12.5 mL of *n*-butyllithium (2 M in hexane) was added over 45 min. The reaction mixture was allowed to warm to −78 °C for 2 h, and a solution of 1-methyl-2-pyrrolidone (1.28 g) in THF (10 mL) was added during 15 min. The reaction mixture was stirred for 2 h at −78 °C, allowed to warm to −20 °C, and poured into 5% HCl (100 mL). This solution was extracted with ether (3 × 75 mL), affording after drying ($MgSO_4$) benzoic acid (0.98 g, 65%) uncontaminated with any *o*-bromobenzoic acid.[12] The aqueous phase was then concentrated to 50 mL, brought to pH 10 with NaOH, and then extracted continuously with CH_2Cl_2. Evaporation of the extract yielded a mixture of shihunine (0.58 g, 23%) and 1-methyl-2-pyrrolidone (100 mg), separated by TLC on alumina PF 254. Crystallization of the former from ether–hexane afforded colorless needles, mp 76–78 °C, identical (mixed melting point, IR, NMR) with an authentic specimen of shihunine obtained from *Dendrobium pierardii*.[3]

The reaction was repeated, and after 2 h at −80 °C D_2O (5 mL) was added to the reaction mixture followed by workup as previously described. The benzoic acid, purified by sublimation, had a MS *m/e* (rel intensity) 124 (2.0), 123 (23.3), 122 (82.1) compared with natural abundance benzoic acid, *m/e* 124 (0.9), 123 (7.6), 122 (90.1), indicating a ratio of unlabeled to monodeuteriobenzoic acid of 87:13. The recovered 1-methyl-2-pyrrolidone (0.7 g) had MS *m/e* (rel intensity) 102 (0.7), 101 (83), 100 (100), 99 (97.4), 98 (22.3), compared with unlabeled material of *m/e* 101 (0.7), 100 (76), 99 (100), 98 (68.0), 97 (0.8), indicating a 74% enrichment of the 1-methyl-2-pyrrolidone with a single deuterium. The ^1H noise-decoupled ^{13}C NMR spectrum of unlabeled 1-methyl-2-pyrrolidone (in $CDCl_3$) was (δ_c, ppm from Me_4Si): C-2 (177.1), C-3 (31.1), C-4 (18.1), C-5 (50.0), NMe (29.7). The ^1H noise-decoupled ^{13}C NMR spectrum of the enriched 1-methyl-2-pyrrolidone was identical except that the signal due to C-3 was a triplet.

Registry No. 1, 6091-64-1; **2**, 872-50-4; **3**, 71819-30-2; **5**, 71819-31-3; **5** picrate, 71819-32-4; **6**, 20323-99-3; **7**, 4031-12-3; **8**, 88-65-3.

(11) (a) Y. Inubushi, Y. Tsuda, T. Konita, and S. Matsumoto, *Chem. Pharm. Bull.*, **12**, 749 (1964); (b) *ibid.*, **16**, 1014 (1968).

(12) The benzoic acid was converted to its methyl ester with diazomethane and analyzed by GLC on 10% Carbowax 20 M on Chromosorb W (60–80 mesh) at 185 °C. With a He flow rate of 25 mL/min the retention times of methyl benzoate and methyl *o*-bromobenzoate were 2.7 and 8.7 min, respectively.

Rearrangement of 2-Diazoceph-3-em 1β-Oxides: Migration of Oxygen from Sulfur to Carbon

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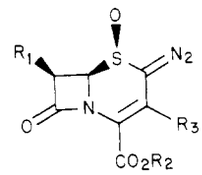
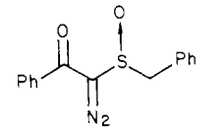
Publications by Bremner and Campbell[1] on the preparation and chemistry of diazosulfoxide **1a** have prompted



1a, R_1 = $C_6H_5OCH_2CONH$; R_2 = CH_2CCl_3; R_3 = CH_3
b, R_1 = $C_6H_5OCH_2CONH$; R_2 = $CH(C_6H_5)_2$; R_3 = CH_2OAc
c, R_1 = H; R_2 = $CH(C_6H_5)_2$; R_3 = CH_3
d, R_1 = H; R_2 = $CH_2OCOC(CH_3)_3$; R_3 = CH_2OAc

us to report our work in this area. We viewed such highly functionalized cephalosporin derivatives as useful for further β-lactam nuclear modification. Specifically, we were interested in examining the behavior of diazosulfoxides such as **1a** in the presence of metal catalysts in order to probe the effect of generating a carbenoid species α to the sulfoxide moiety. Hodson and Holt,[2] in an unsuccessful attempt to prepare a similar but less complex α-diazo-β-ketosulfoxide **2** by diazo transfer, isolated **3** and postulated



2

its formation via an intramolecular rearrangement, giving intermediate thiol ester **4** (not isolated or characterized).

(1) (a) Bremner, D. H.; Campbell, M. M. *J. Chem. Soc., Chem. Commun.* **1976**, 538. (b) Bremner, D. H.; Campbell, M. M. *J. Chem. Soc. Perkin Trans. 1* **1977**, 2298.

(2) Hodson, D.; Holt, G. *J. Chem. Soc. C* **1968**, 1602.

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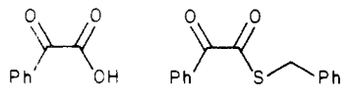
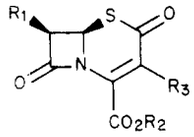


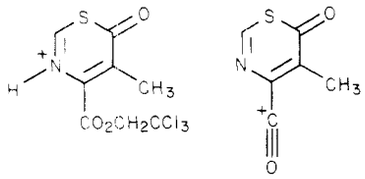
3 4

An analogous rearrangement[3] with 1 would produce 2-oxocephalosporin **5** and would constitute a facile synthesis of a potentially interesting structural type.[4,5]



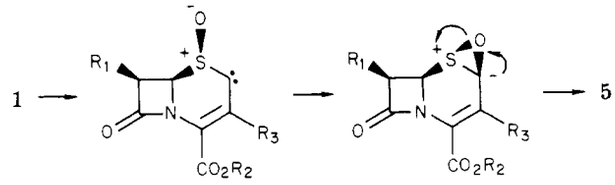
5a, $R_1 = C_6H_5OCH_2CONH$; $R_2 = CH_2CCl_3$; $R_3 = CH_3$
b, $R_1 = C_6H_5OCH_2CONH$; $R_2 = CH(C_6H_5)_2$; $R_3 = CH_2OAc$
c, $R_1 = H$; $R_2 = CH(C_6H_5)_2$; $R_3 = CH_3$
d, $R_1 = H$; $R_2 = CH_2OCOC(CH_3)_3$; $R_3 = CH_2OAc$
e, $R_1 = C_6H_5OCH_2CONH$; $R_2 = H$; $R_3 = CH_2OAc$

When rhodium acetate (5% by weight) was added to a THF solution of **1a** at 0 °C, vigorous nitrogen evolution resulted. Silica gel chromatography of the crude reaction mixture afforded a 40% yield of 2′,2′,2′-trichloroethyl 2-oxo-3-methyl-7β-(phenoxyacetamido)ceph-3-em-4-carboxylate (**5a**) isolated as a foam. Crystallization from chloroform/hexane yielded an analytically pure sample (mp 147–148°), which possessed the correct elemental analysis and spectral data consistent with the structure as shown. The mass spectrum exhibited no parent ion but did give intense ions at *m/e* 302, 304, and 306 and at *m/e* 154, corresponding to elemental compositions of $C_8H_7Cl_3NO_3S$ and $C_6H_4NO_2S$, respectively (confirmed by high-resolution spectrum). These ions are characteristic of cephems[6] and were assigned the following structures:



In a study of the scope of this novel rearrangement, previously unknown diazocephems **1b**, **1c**, and **1d** were synthesized by diazo transfer and then subjected to the rhodium acetate conditions to afford 2-oxoceph-3-ems **5b**, **5c**, and **5d**, respectively. The ^{13}C NMR of **5b** possessed signals for the carbonyl carbons at 183.32, 169.78, 168.55, 161.06, and 159.30 ppm; on the basis of comparison with suitable models, the signal at 183.32 ppm is assigned to the thiol lactone carbonyl carbon atom.

While the mechanism of formation of **5a** has not been studied, we suggest that initially formed carbenoid intermediate **6** undergoes an intramolecular cyclization to yield ylide **7**[7] with subsequent bond reorganization to **5**.[8]



6 7

The nature of the metal catalyst seems to play an important role. Campbell[1b] reported that treatment of **1a** with copper salts led to β-lactam destruction. In addition, we have found that palladium acetate failed to catalyze the diazo decomposition of **1a**. The apparent specificity for rhodium salts observed thus far is the subject of continued study.

Ester **5b** was deblocked at 0 °C by using trifluoroacetic acid/anisole in CH_2Cl_2 solution. The resulting 2-oxocephalosporin **5e** exhibited a low order of antibiotic activity against a wide variety of organisms.[9]

Experimental Section

Melting points (uncorrected) were determined with a Thomas-Hoover capillary apparatus. NMR spectra were recorded with a Varian T-60 spectrometer using tetramethylsilane (Me_4Si) as an internal standard. ^{13}C NMR spectra were obtained in the FFT mode on a Varian XL-100-15 (25 MHz) spectrometer equipped with a Nicolet Technology 1080 data system. Chemical shifts are reported in parts per million relative to Me_4Si as an internal standard. Mass spectra were recorded with an AEI MS-30 spectrometer equipped with a D5-50 data system. TLC was performed by using precoated 0.25 mm thick silica gel 60 plates (Merck) and column chromatography with silica gel (Merck, 70-230 mesh). Infrared spectra (IR) were recorded on a Perkin-Elmer 237B spectrophotometer, and ultraviolet spectra (UV) were obtained on a Beckman DB spectrophotometer.

General Procedure for Preparation of 2-Diazoceph-3-em 1β-Oxides (1). To a stirred solution of 1 mmol of the corresponding ceph-3-em 1β-oxide and 2 mmol of diisopropylethylamine in 25 mL of methylene chloride at 0 °C was added 2 mmol of picryl azide.[10,11] The reaction was allowed to proceed at 0 °C for 2 h and then evaporated to dryness. The crude reaction mixture was chromatographed on silica gel by using a methylene chloride–ethyl acetate gradient to afford 1.

1a: 85% yield; mp 110 °C dec (lit.[1b] mp 89–90 °C dec); IR (CH_2Cl_2) 2080, 1800, 1725, 1680 cm^{-1}.

1b: 36% yield; R_f 0.2 (4:1 $CHCl_3$–AcOEt); IR (CH_2Cl_2) 2080, 1805, 1745, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0 (s, 3 H), 4.5 (m, 3 H), 4.8 and 5.4 (AB q, 2 H, J = 13 Hz), 6.2 (dd, 1 H, J = 5, 10 Hz), 6.8–7.6 (m, 11 H), 7.8 (d, 1 H, J = 10 Hz).

1c: 48% yield; R_f 0.4 (4:1 $CHCl_3$–AcOEt); IR (CH_2Cl_2) 2075, 1790, 1710 cm^{-1}; ^1H NMR (Me_2SO-d_6) δ 2.2 (s, 3 H), 3.5 (m, 2 H), 4.9 (dd, 1 H, J = 2, 5 Hz), 6.8 (s, 1 H), 7.0–7.6 (m, 10 H).

1d: 69.5% yield; R_f 0.8 (AcOEt); IR (CH_2Cl_2) 2070, 1790, 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2 (s, 9 H), 2.1 (s, 3 H), 3.0–4.0 (m, 2 H), 4.7 (m, 1 H), 4.8 and 5.6 (AB q, 2 H, J = 13 Hz), 5.8 and 6.0 (AB q, 2 H, J = 5 Hz).

General Procedure for the Preparation of 2-Oxoceph-3-ems (5). To a stirred solution of 1 mmol of the corresponding 2-diazoceph-3-em 1β-oxide (1) in 10 mL of tetrahydrofuran at 0 °C was added 5% by weight of rhodium(II) acetate dimer. Vigorous nitrogen evolution occurred. After 0.5 h the reaction was evaporated to dryness and chromatographed on silica gel by

(3) On the other hand, it should be noted that no oxygen migration was reported in Venier's studies of the uncatalyzed decomposition of phenylsulfinyldiazomethane. See: Venier, C. G.; Barager, H. J., III; Ward, M. A. *J. Am. Chem. Soc.* **1975**, *97*, 3238. Venier, C. G.; Ward, M. A. *Tetrahedron Lett.* **1978**, 3215.

(4) Antibacterial activity has been reported for 2-methylenecephalosporins. See: Wright, I. G.; Ashbrook, C. W.; Goodson, T.; Kaiser, G. V.; Van Heyningen, E. M. *J. Med. Chem.* **1971**, *14*, 420.

(5) A totally synthetic 2-oxocephalosporin with the important Δ-3 double bond reduced has been reported. See: Flynn, E. H., Ed.; "Cephalosporins and Penicillins: Chemistry and Biology"; Academic Press: New York, 1972; p 276.

(6) Flynn, E. H., Ed.; "Cephalosporins and Penicillins: Chemistry and Biology"; Academic Press: New York, 1972; p 326.

(7) This rearrangement can be considered to be an intramolecular version of the reaction type exemplified by the deoxygenation of *N*-oxides by carbenes. See: Schweizer, E. E.; O'Neill, G. J. *J. Org. Chem.* **1963**, *28*, 2460. Schweizer, E. E.; O'Neill, G. J.; Wemple, J. N. *Ibid.* **1964**, *29*, 1744.

(8) A bridged species isoelectronic with the oxathiirane moiety of **7** has been proposed to explain the results of the carbenic decomposition of a diazosulfide. See: Robson, J. H.; Shechter, H. *J. Am. Chem. Soc.* **1967**, *89*, 7112.

(9) After this manuscript was completed, there appeared a report on the synthesis (by an independent route) of 2-oxocephalosporins that described the thienylacetamido analogue of **5e**. See: Kim, C. U.; Misco, P. F.; McGregor, D. N. *J. Med. Chem.* **1979**, *22*, 743.

(10) Picryl azide is an effective diazo transfer reagent (unpublished observations of E. J. Corey and A. M. Felix).

(11) Schrader, E. *Chem. Ber.* **1917**, *50*, 777.

(12) Scartazzini, R. *Helv. Chim. Acta* **1977**, *60*, 1510.

employing a methylene chloride–ethyl acetate gradient to afford **5**.

5a: 40% yield; mp 147–148 °C (from chloroform–hexane); IR (CH_2Cl_2) 1800 (β-lactam), 1750 (ester), 1685 (amide), 1645 cm^{-1} (thiol lactone); ^1H NMR ($CDCl_3$) δ 2.2 (s, 3 H, CH_3), 4.6 (s, 2 H, CH_2O), 5.0 (s, 2 H, CH_2CCl_3), 5.8–6.1 (m, 2 H, H-6/H-7), 6.8–7.5 (m, 5 H, Ph), 7.7 (d, 1 H, J = 8 Hz, NH); $[\alpha]^{25}_D$ –91° (c 1, CH_2Cl_2); UV (CH_2Cl_2) λ_{max} 312 (ϵ 7400). Anal. Calcd for $C_{18}H_{15}Cl_3N_2O_6S$: C, 43.78; H, 3.06; N, 5.67. Found: C, 44.05; H, 3.25; N, 5.79.

5b: 38% yield; R_f 0.9 (9:1 $CHCl_3$–AcOEt); IR (CH_2Cl_2) 1800, 1740, 1680, 1645 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.8 (s, 3 H), 4.6 (s, 2 H), 4.8 and 5.1 (AB q, 2 H, J = 12 Hz), 5.8–6.1 (m, 2 H, H-6/H-7), 6.8–7.9 (m, 12 H); $[\alpha]^{25}_D$ –110° (c 1, CH_2Cl_2); UV (CH_2Cl_2) λ_{max} 308 (ϵ 6000).

5c: 10% yield; R_f 0.8 (4:1 $CHCl_3$–AcOEt); IR (CH_2Cl_2) 1785, 1730, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.97 (s, 3 H), 3.0–4.0 (m, 2 H), 5.55 (dd, 1 H, J = 2, 5 Hz), 7.1 (s, 1 H), 7.0–7.6 (m, 10 H).

5d: 26% yield; R_f 0.9 (4:1 $CHCl_3$–AcOEt); IR (CH_2Cl_2) 1800, 1750, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (s, 9 H), 2.05 (s, 3 H), 3.2–4.05 (m, 2 H), 4.8 and 5.2 (AB q, 2 H, J = 12 Hz), 5.6 (dd, 1 H, J = 3, 6 Hz), 6.0 (s, 2 H).

2-Oxo-3-(acetoxymethyl)-7β-(phenoxyacetamido)ceph-3-em-4-carboxylic Acid (5e). To a solution of 98 mg (0.17 mmol) of **5b** in 15 mL of methylene chloride at 0 °C were added 90 mg (0.84 mmol) of anisole and 743 mg (6.52 mmol) of trifluoroacetic acid.[11] After 0.5 h at 0 °C the reaction was diluted with 50 mL of ice-cold toluene and evaporated to dryness. The residue was dissolved in methylene chloride, treated with 17 mg (0.17 mmol) of triethylamine, and again evaporated to dryness. Trituration with ether afforded 45 mg of **5e** as the amorphous triethylamine salt (54%): IR (CH_2Cl_2) 1780, 1650, 1640, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0 (s, 3 H), 4.5 (s, 2 H), 4.8 and 5.2 (AB q, 2 H, J = 12 Hz), 5.8–6.0 (m, 2 H), 6.8–7.6 (m, 6 H).

Acknowledgment. The authors wish to thank Professor E. J. Corey for helpful discussions.

Registry No. **1a**, 66614-35-5; **1b**, 71786-01-1; **1c**, 71786-02-2; **1d**, 71786-03-3; **5a**, 71786-04-4; **5b**, 71786-05-5; **5c**, 71786-06-6; **5d**, 71786-07-7; **5e**, 71786-08-8; 2,2,2-trichloroethyl 1β-oxo-3-methyl-7β-(phenoxyacetamido)ceph-3-em-4-carboxylate, 24689-52-9; diphenylmethyl 1β-oxo-3-(acetoxymethyl)-7β-(phenoxyacetamido)-ceph-3-em-4-carboxylate, 71786-09-9; diphenylmethyl 1β-oxo-3-methylceph-3-em-4-carboxylate, 71786-10-2; *tert*-butyl(carbonyloxy)methyl 1β-oxo-3-(acetoxymethyl)ceph-3-em-4-carboxylate, 71786-11-3.

Regiospecific Dimerization Leading to a 14-Membered Heterocyclic Ring. Synthesis and X-ray Structure

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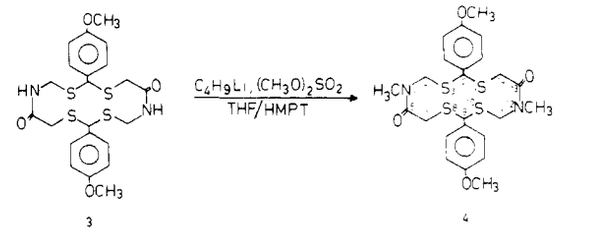
Received August 6, 1979

In connection with work related to natural products of the gliotoxin–sporidesmin class of compounds,[1] we became interested in studying simple 4-aza-1,2-dithian-5-ones.

An approach involving preparation of *N*-(thiomethyl)-thioglycolic acid amide (**2**), followed by protection of the thiol functions along the route used by Kishi et al.[2] seemed to be promising, but in our case the outcome, although not entirely unexpected, was not the desired one.

We prepared *N*-[(acetylthio)methyl](acetylthio)acetic acid amide **1** through the reaction of *N*-(chloromethyl)-chloroacetamide[3] with potassium thioacetate. From **1** the dithiol **2** was obtained by hydrolysis with 1.2 N methanolic hydrochloric acid. When **2** was reacted with anisaldehyde



and small amounts of boron trifluoride etherate in methylene chloride,[2] a compound **3** was obtained in 61% yield. This highly insoluble compound was converted to a more soluble derivative by treatment of a solution of **3** in HMPA/THF (hexamethylphosphorictriamide/tetrahydrofuran) cooled to –95 °C with butyllithium and then with dimethyl sulfate, which gave the N-methylated derivative **4** in good yield.

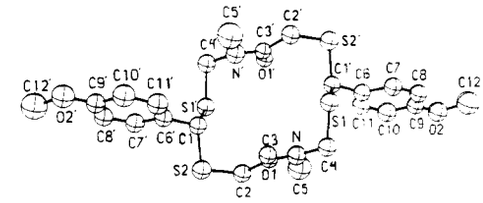


Figure 1. Computer-generated drawing of the X-ray model of **4**.

An X-ray crystal structure determination undertaken for **4** showed unequivocally that this compound is dimeric (see Figure 1), being 2,9-bis(*p*-methoxyphenyl)-5,12-dimethyl-5,12-diaza-1,3,8,10-tetrathiacyclotetradecane-6,13-dione, **3** thus being 2,9-bis(*p*-methoxyphenyl)-5,12-diaza-1,3,8,10-tetrathiacyclotetradecane-6,13-dione.

4 was recrystallized from chloroform. The very thin, nearly square crystals are orthorhombic with a = 9.171 (4), b = 29.049 (4), and c = 9.593 (13) Å. Systematic extinctions indicate space group *Pbca*, with Z = 4. The structure, determined from 1801 graphite-monochromatized Cu Kα reflections, measured at –125 °C (isotropic temperature factors, no H atoms), was solved by symbolic addition and refined by full-matrix least-squares methods to R = 0.12. Despite the low-temperature data many of the thermal parameters are quite high (B = 4–8 Å^2), but all geometric parameters are within normal ranges (see supplementary material).

Compound **3** gave correct analysis for the desired thioacetal, and a very weak peak at m/e 510 in its mass spectrum is also consistent with the dimeric structure. The mass spectrum of **4** also gave some evidence for a dimeric structure: m/e (11 eV) 538 (6.3%).

An interesting point is that, in accordance with the X-ray crystal structure determination, only one of two possible dimeric products was formed. The exclusive formation of **3** might be due to dimerization of intermediates of either type **5** or type **6** and indicates a large difference in the nucleophilicity of the SH groups of **2**.

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(1) P. W. Trown, *Biochem. Res.*, **33**, 402 (1968).
(2) Y. Kishi, T. Kukugama, and S. Nakatsuka, *J. Am. Chem. Soc.*, **95**, 6490 (1973).
(3) M. Pranka and D. J. Polton, British Patent 917 924 (1963); *Chem. Abstr.*, **59**, 1488*a* (1963).

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