mL of brine, and dried over anhydrous $MgSO_4$.

Crude **4a**, obtained by using the different reducing agents, was purified by preparative TLC (silica gel) with 20% ether in hexane as eluant to obtain **4a**. Compound (+)-**4a** was crystallized from *n*-hexane: mp 99 °C; IR (KBr) 3430 cm^{-1} (broad, OH); ^1H NMR ($CDCl_3$) δ 7.40–7.10 (m, 10 H), 4.94 (d, J = 4.5 Hz, *erythro* PhCH), 4.35 (d, 1 H, J = 4.5 Hz *erythro* (PhCH), 3.26 (s, 3 H, *erythro* MeO), 2.6 (br s, 1 H, OH); $[\alpha]_D$ +23.4° (*c* 1.6, $CHCl_3$); EI-MS, *m/z* (relative intensity) 228 (M^+) 211 (M^+ - OH, 1), 121 (100), 91 (7), 77 (14).

threo Isomer: ^1H NMR ($CDCl_3$) δ 4.6 (d, 1 H, J = 7 Hz, *threo* PhCH), 3.34 (s, 3 H, *threo* MeO). Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.71; H, 7.06. Found: C, 78.71; H, 7.08.

Reduction with DIBAL. A solution of 0.438 g (1.94 mmol) of **3a** in 15 mL of dry THF was cooled to −78 °C under nitrogen. DIBAL in hexane, 5.8 mL (5.8 mmol), was added to the reaction mixture via syringe, and the mixture was stirred for 2 h. After being quenched by cautious addition of 3 mL of water, the reaction mixture was diluted with 20 mL of ether, transferred to a separatory funnel, washed with 1 N HCl (2 × 10 mL) and 10 mL of brine, and dried over anhydrous $MgSO_4$. After removal of the solvent the crude **4a** was crystallized from *n*-hexane to give 0.380 g (85%) of (+)-**4a**, mp 99–100 °C.

(+)-*erythro*-α,β-Diphenyl-β-hydroxyethanol Benzyl Ether (4b). As described above 0.080 g (0.265 mmol) of **3b** in 5 mL of THF was reduced with 0.8 mL (0.8 mmol) of DIBAL in *n*-hexane at −78 °C. After the reaction was quenched by addition of 1 mL of water, the mixture was diluted with 10 mL of ether, transferred to a separatory funnel, washed with 1 N HCl (2 × 5 mL) and 5 mL of brine, and dried over anhydrous $MgSO_4$. Removal of the solvent gives 0.063 g (77%) of **4b**, which is crystallized from *n*-hexane: mp 59 °C; IR (neat) 3420 (OH) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45–7.05 (m, 15 H), 4.92 (d, J = 5 Hz, erythro PhCH), 4.58–4.15 (m, 3 H), 2.25 (br s, 1 H); $[\alpha]_D$ +23.7° (*c* 1.9, $CHCl_3$).

threo Isomer: ^1H NMR ($CDCl_3$) δ 7.5–6.9 (m, 15 H, 4.67 (d, 1 H, J = 7 Hz, *threo* PhCH), 3.34. Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.87; H, 6.62. Found: C, 82.64; H, 6.65.

(+)-(*S*)-Benzoin Oxime (9). To 0.4 g (5.76 mmol) of hydroxylamine hydrochloride were added 0.8 g (5.87 mmol) sodium acetate and 0.5 g (2.36 mmol) of (+)-(*S*)-benzoin (**2**) in 15 mL of ethanol. Enough water (3 mL) to dissolve the solids was added, and the solution was heated at reflux for 20 min. After the mixture was cooled to room temperature, 25 mL of water was added, and the flask was placed in an ice bath. After 20 min, the white crystals were collected and air-dried to give 0.5 g (90%) of (+)-(*S*)-benzoin oxime (**9**) as a 63:37 *E*:*Z* mixture, determined by ^1H NMR:[16] mp 145–153 °C (lit.[17] mp 163 °C); ^1H NMR ($CDCl_3$) δ 7.55–7.2 (m, 10 H), 6.2 (s, PhC*H*, 0.37 H, *Z* isomer), 5.59 (s, 0.63 H, *E* isomer), 3.7 (br s, 1 H, OH); $[\alpha]_D$ +2.6° (*c* 0.5, $CHCl_3$) [lit.[6] $[\alpha]_D$ +3.2° (*c* 0.5, $CHCl_3$) of the (−)-(*R*)-(*E*)-**9**].

(+)-*erythro*-α,β-Diphenyl-β-hydroxyamine (10). (+)-(*S*)-Benzoin oxime (**9**), 0.5 g (2.2 mmol), was hydrogenated over 5% Pd/C catalyst in 10 mL of ethanol containing 1.5% HCl for 7 h according to the procedure of Tishler et al.[17] to give 0.32 g (69%) of **10**: mp 135–6 °C (lit.[13] mp 143 °C); HCl salt, mp 208–209 °C (lit. mp 210–212 °C); $[\alpha]_D$ +66.8° (*c* 0.5, $CHCl_3$) [lit.[13] $[\alpha]_D$ +69.6° (*c* 0.65, H_2O)]; ^1H NMR ($CDCl_3$) δ 7.35–7.15 (m, 10 H), 4.75 (d, 2 H, J = 5 Hz), 4.15 (d, 1 H, J = 5 Hz), 2.1–1.6 (br s, 3 H, OH, NH_2).

Acknowledgment. This work was supported by the National Institutes of Health (Institute of General Medical Sciences) through Grant GM-34014.

Registry No. **1**, 451-40-1; (+)-**2**, 5928-67-6; (+)-**2** trifluoroacetate, 118298-90-1; (+)-**3a**, 82572-27-8; (±)-**3a**, 5987-95-1; (+)-**3b**, 118298-91-2; (+)-**4a**, 118353-44-9; **4a** threo isomer, 118353-46-1; (+)-**4b**, 118298-93-4; **4b** threo isomer, 118298-94-5; (+)-**5**, 104322-63-6; (−)-**6**, 60886-80-8; **8a**, 118298-89-8; **8b**, 118298-92-3; (+)-**9** E isomer, 118353-45-0; (+)-**9** Z isomer, 118353-47-2; (+)-**10**, 23364-44-5; sodium bis(trimethylsilyl)amide, 1070-89-9; benzyl trichloroacetimidate, 81927-55-1; benzyl bromide, 100-39-0.

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Structural Studies on the Product of Heterocyclization of 2,5-Dimercapto-1,3,4-thiadiazole with 1,3-Dibromopropane: A Revision

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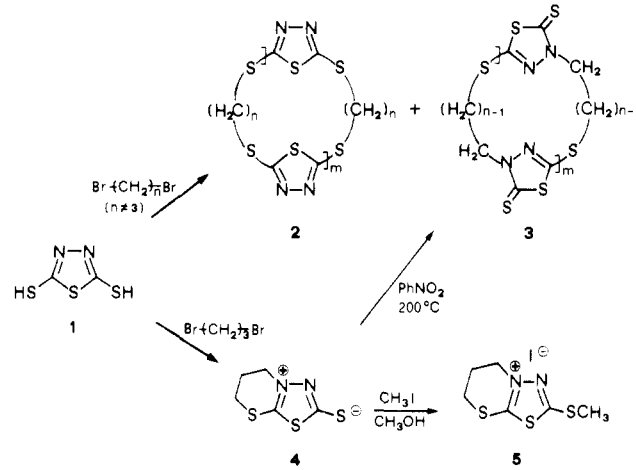
We have been interested in the synthesis and stereochemical behavior of medium-sized S-bridged metacyclophanes[1] and heterophanes.[2] Their conformational aspects in solution have been well-studied via the convenient ^1H NMR spectral probes present in the form of "internal" protons or substituents.[3]

Recently, we have shown that the high-dilution heterocyclization of 2,5-dimercapto-1,3,4-thiadiazole (**1**) with 1,ω-dibromoalkanes $Br(CH_2)_nBr$ (n = 1–4) in alkaline medium offers a practical route to polythia[$(n + 2)_m$]-(2,5)-1,3,4-thiadiazolophanes **2** and/or [$(n + 1)_m$](3,5)-1,3,4-thiadiazolinophanethiones **3**. Since heterophanes **2** and **3** lack the above ^1H NMR spectral probes, single-crystal X-ray structure determinations on the products of heterocyclization of **1** with 1,3-dibromopropane (n = 3) and 1,4-dibromobutane (n = 4) have been conducted in order to establish their solid-state conformations. With the aid of this study, the revised structure (**4**) is now reported for the former product.



Results and Discussion

The structural data of **2** (m = 1; n = 4) have been already reported.[5] Quite surprisingly, structural analysis on the product of the reaction of the dipotassium salt of **1** with 1,3-dibromopropane has shown it to be the monomer **4**, not the dimer **3** (m = 1; n = 3). Coordinates of **4** are given in Table I, and the molecule is illustrated in Figure 1. The molecule lies on a mirror plane, with the atoms C(4) and C(5) of the six-membered thiazine ring disordered into half-populated positions related by the mirror. Except for the disordered C atoms, the molecule is exactly planar, and all molecules pack in parallel fashion in the crystal.

The molecule is characterized as a zwitterion on the basis of the planarity of the heterocyclic thiadiazole ring and

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Table I. Positional Parameters and Their Estimated Standard Deviations for 4[a]

atom	x	y	z	B_{eq} or B
S(1)	0.3655 (1)	1/4	0.5898 (2)	4.37 (4)
S(2)	0.5749 (1)	1/4	0.7293 (2)	4.54 (4)
S(3)	0.2365 (1)	1/4	0.2922 (2)	4.67 (4)
N(1)	0.5249 (3)	1/4	0.4163 (6)	3.5 (1)
N(2)	0.4414 (3)	1/4	0.3182 (5)	3.2 (1)
C(1)	0.4985 (4)	1/4	0.5679 (7)	3.3 (1)
C(2)	0.3518 (4)	1/4	0.3867 (7)	3.3 (1)
C(3)	0.4633 (5)	1/4	0.1428 (7)	4.6 (2)
C(4)	0.3682 (6)	0.324 (1)	0.0505 (9)	4.9 (3)
C(5)	0.2791 (6)	0.198 (1)	0.0859 (9)	3.7 (2)*

[a] Starred atom was refined isotropically. C(4) and C(5) have population = 1/2. Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

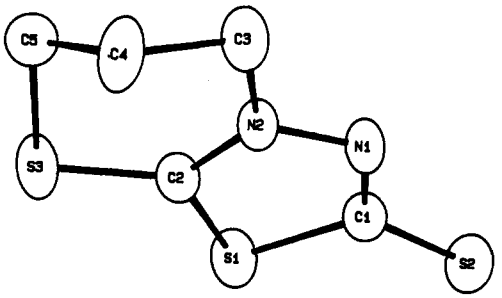

Figure 1. ORTEP drawing of 4 with the numbering scheme.

certain bond lengths. The C(2)—N(2) bond has length 1.316 (7) Å, indicative of significant double-bond character, and the C(1)—S(2) bond has a length of 1.682 (6) Å, shorter than a typical C_{sp^2}—S bond such as C(2)—S(3) [1.718 (6) Å], but longer than a bona fide C=S bond, such as the 1.657 (2) Å found in the related molecule 15⟨O_3-(3,5)1,3,4-thiadiazolino,S-coronand-5⟩-15-thione.[6,7]

Remarkably, the C(5)–S(3) bond length [1.846 (8) Å] is significantly longer than that [1.820 (4) Å] found in the thiazine ring of 2,3,4,5-tetrahydro-7,7-diphenylimidazo-[2,1-*b*]thiazine-6(7*H*)-one.[8] This finding may not only account for the great chemical reactivity of the thiazine ring in this system (i.e., regioselective ring-opening reactions by nucleophilic agents)[4] but also be responsible for the previous wrong structural assignment for **4**. In fact, in the original report, the molecular formula was deduced from the highest observable ion (*m/z* 380, 6.4% relative intensity) in the 18-eV mass spectrum of **4**. In retrospect, the peak at *m/z* 380 can be explained in two ways: (i) **4** thermally dimerizes under MS conditions or (ii) its nature is such that it volatilizes as clusters. In agreement with the first hypothesis, zwitterion **4** undergoes thermal dimerization to 1,10-dithia[4.4](3,5)-1,3,4-thiadiazolinophane-6,15-dithione **3** (*m* = 1; *n* = 3) by heating in nitrobenzene for several hours. Besides, **4** is easily converted to the *S*-methyl 1,3,4-thiadiazolium cation **5** by treatment with CH_3I in methanol. It is noteworthy that the ^1H NMR spectrum of iodide **5** closely matches that of the corresponding bromide (referred to as compound **40** in ref 4), obtained by a different synthetic route.

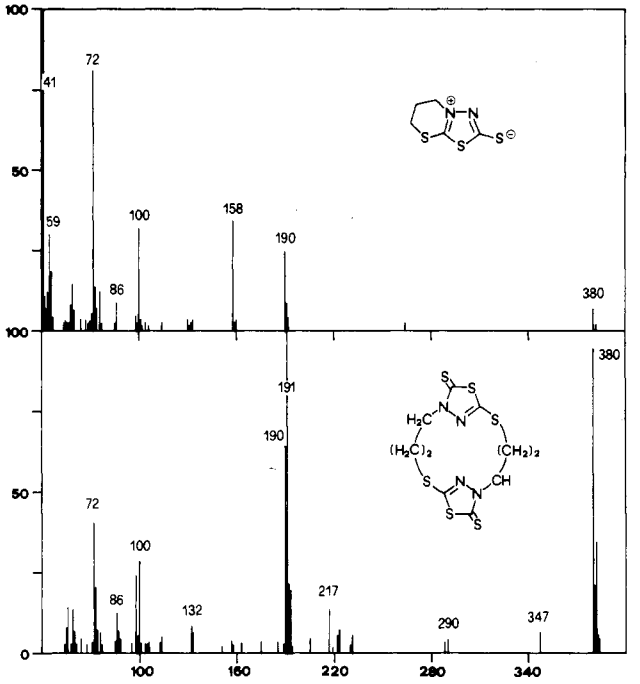

Figure 2. The 18-eV mass spectra of zwitterion **4** (monomer) and of macrocycle **3** (*m* = 1; *n* = 3) (dimer).

A comparison of the 18-eV mass spectra of mesoionic bicyclic 1,3,4-thiadiazole-2-thione **4** and its cyclic dimer **3** (*m* = 1; *n* = 3) is shown in Figure 2. In the latter compound, the molecular ion at *m/z* 380 is now the second-largest peak in the spectrum (94% relative intensity), while characteristic $[M - SH]^+$ and $[M/2 + 1]^+$ fragment ions at *m/z* 347 (6.7% relative intensity) and 191 (base peak) are also present. As might be expected, salt **5**, in which the zwitterionic nature of **4** has been destroyed, showed the molecular ion peak at *m/z* 332 (31% relative intensity).

Experimental Section

Melting points were determined on a Kofler apparatus and are uncorrected. ^1H NMR spectra were recorded on a Bruker WP-80 NMR spectrometer, using Me_4Si as an internal standard. Mass spectra were determined on a Kratos MS 50 double-focusing mass spectrometer operating at 18 eV.

Thermal Dimerization of 4 to 3 (*m* = 1; *n* = 3). A stirred solution of **4** (described as compound **37** in ref 4) (50 mg) in nitrobenzene (5 mL) was refluxed under N_2 for 24 h. The reaction produced a light brown precipitate, which was recrystallized twice from dimethyl sulfoxide to afford 1,10-dithia[4.4](3,5)-1,3,4-thiadiazolinophane-6,15-dithione **3** (*m* = 1; *n* = 3) as almost colorless prisms: 8 mg, 16%; mp 272–276 °C; ^1H NMR (DMSO-d_6) δ 2.27 (m, $SCH_2CH_2CH_2N$, 4 H), 3.27 (dd, *J* = 5.6 Hz, $SCH_2CH_2CH_2N$, 4 H), and 4.34 (t, *J* = 5.6 Hz, $SCH_2CH_2CH_2N$, 4 H). Anal. Calcd for $C_{10}H_{12}N_4S_6$: C, 31.55; H, 3.18; N, 14.72. Found: C, 31.24; H, 3.09; N, 14.88.

4,5-Dihydro-1,3-thiazino[2,3-*b*][1,3,4]thiadiazolium Iodide 5. A slurry of **4** (0.19 g, 1 mmol) and methyl iodide (1 mL) in methanol (10 mL) was stirred at room temperature until disso-

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lution had occurred. The mixture was then heated at reflux for 0.5 h and cooled. The solvent was evaporated, and the residue was recrystallized from absolute ethanol to give salt **5** as white crystals: 0.25 g, 75%; ^{1}H NMR (CD_3OD) δ 2.62 (m, $SCH_2CH_2CH_2N$, 2 H), 2.82 (s, SCH_3, 3 H), 3.60 (t, J = 5.7 Hz, $SCH_2CH_2CH_2N$, 2 H), and 4.63 (t, J = 5.7 Hz, $SCH_2CH_2CH_2N$, 2 H). Anal. Calcd for $C_6H_9IN_2S_3$: C, 21.69; H, 2.74; N, 8.43. Found: C, 21.85; H, 2.83; N, 8.30.

X-ray Structure Determination of 4. X-ray data of **4** were collected by using a pale yellow crystal of dimensions 0.08 × 0.15 × 0.38 mm on an Enraf-Nonius CAD4 diffractometer equipped with Cu Kα radiation (λ = 1.541 84 Å) and a graphite monochromator. Crystal data are as follows: $C_5H_6N_2S_3$, fw = 190.3, orthorhombic space group P_{nma}, a = 13.241 (2) Å, b = 7.080 (1) Å, c = 8.330 (2) Å, V = 780.9 (4) Å^3, Z = 4, D_{calcd} = 1.619 g cm^{-3} at T = 25 °C, μ = 79.6 cm^{-1}. One octant of data having 4° < 2θ < 150° was collected by ω–2θ scans. Data reduction included corrections for background, Lorentz, polarization, and absorption. Absorption corrections were based on psi scans, and the minimum relative transmission coefficient was 82.9%. Of 875 unique data, 749 had $I > 3\sigma(I)$ and were used in the refinement.

The structure was solved by direct methods in the centrosymmetric space group, yielding a model in which the molecule lies on the crystallographic mirror plane. Two of the C atoms of the six-membered heterocyclic ring are disordered into half-populated positions related by the mirror. C(4) lies 0.52 Å from the mirror; thus the two half-atoms are sufficiently resolved to allow anisotropic refinement. C(5) lies only 0.37 Å from the mirror and was refined anisotropically. All other non-hydrogen atoms were refined anisotropically, while H atoms were neither located nor included in the refinement. Least squares was based on F with weights $w = \sigma^{-2}(F_o)$ and varied 63 parameters. At convergence, R = 0.046, R_w = 0.055, and maximum residual density was 0.47 e Å^{-3}. Refinement of ordered models in noncentrosymmetric space group P_{na2_1} led to high correlations and chemically unreasonable, divergent results.

Acknowledgment. We thank the Italian Ministry of Education for partial support of this work.

Registry No. **3**, 105785-10-2; **4**, 119366-95-9; **5**, 119366-96-0.

Supplementary Material Available: The packing of the molecules of **4** in the unit cell and tables of the anisotropic thermal parameters, bond distances, bond angles, and torsion angles (5 pages). Ordering information is given on any current masthead page.

Additions and Corrections

Vol. 53, 1988

Mohamad B. Ksebati, Francis J. Schmitz,* and Sarath P. Gunasekera. Pouosides A–E, Novel Triterpene Galactosides from a Marine Sponge, *Asteropus* sp..

Pages 3919–3920. Figure 1 consists of three parts: 1a, 1b, and 1c. The legend under Figures 1 is for Figure 1a. The legends for Figures 2 and 3 should be part of the legend for Figure 1 and should be listed as Figure 1b and Figure 1c, respectively. Figure 2 legend should read "Results from long-range ^{1}H/^{13}C correlation experiments." Figure 3 legend should read "Partial Structures."

Shiv Kumar and Nelson J. Leonard*. Nucleoside Annelating Agents: Structures and Electrophilic Behavior of the Products Formed with *N*-Chlorocarbonyl Isocyanate.

Page 3959. The last sentence on the page should read: "The annelation of unsaturated six-membered rings onto pyrimidine and purine bases and nucleosides has also been reported.[4,29,67]"

Footnote 67 should be added:

(67) Olomucki, M.; Le Gall, J. Y.; Colinart, S.; Durant, F.; Norberg, B.; Evrard, G. *Tetrahedron Lett.* **1984**, *25*, 3471. Thomé, F.; Blois, F.; Olomucki, A.; Olomucki, M. *Eur. J. Biochem.* **1987**, *162*, 433. Roques, P.; Olomucki, M. *Eur. J. Biochem.* **1987**, *167*, 103. Roques, P.; Olomucki, M. *Biochem. Pharmacol.* **1988**, *37*, 1823.

Kazuaki Sukata. Efficient Synthesis of Silyl Azides Using Sodium Azide Impregnated on Amberlite XAD Resin.

Page 4868. The captions for Figures 1 and 2 should be interchanged.