means of ^{31}P NMR spectrometry using the special system of vacuum vessels shown in Figure 2. The ammonium salt of phosphorothioic acid (1×10^{-4} mol) was placed in part 1 of Figure 2. The system was connected to a vacuum line and evacuated before methylene chloride (2 mL) was distilled into the NMR tube (part 1 of the system). The tube was closed with a Teflon stopcock (no. 5), and 5×10^{-4} mol of the same base was stored in reservoir 4. This sample was analogously dissolved in the mixture (10 mL) of CH_2Cl_2 and TFA (273.6 mg, 2.4×10^{-3} mol). The vessel (part 4) was immersed in liquid nitrogen and sealed under vacuum with a flame. The system allows for the gradual change of concentration of TFA in tube 1 without affecting of the concentration of phosphorothioate in tube 1. The desired portion of the acidic solution was added from reservoir 4 through buret 3 to the solution in the tube 1 before each measurement of the chemical shift was performed. This operation was sequentially repeated.

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Registry No. (*R*)-**1**, 71719-69-2; (*S*)-**1**, 75716-63-1; **2**, 75716-64-2; **3**, 75716-65-3; (*R*)-**6**, 71719-72-7; (*S*)-**6**, 71719-71-6; **7**, 45734-11-0; **8**, 75716-66-4; **9**, 75716-67-5; *O,O*-dimethyl phosphorothioic acid dicyclohexylammonium salt, 13941-61-2; dimethyl phosphonate, 868-85-9; 2-hydroxy-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane methyltriethylammonium salt, 75716-68-6; 2-methoxy-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane, 1005-97-6.

Synthesis and Conformational Properties of *N,N*-Dialkyl-6,7-dihydro-5*H*-dibenzo[*b,g*][1,5]thiazocinium Salts[1]

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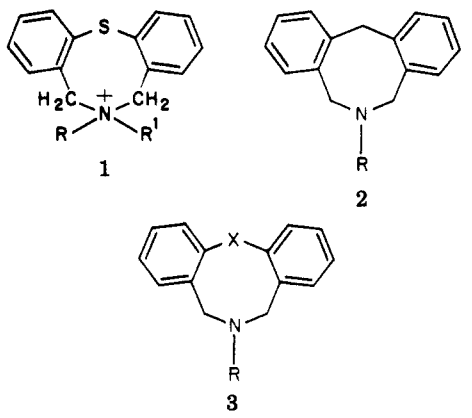
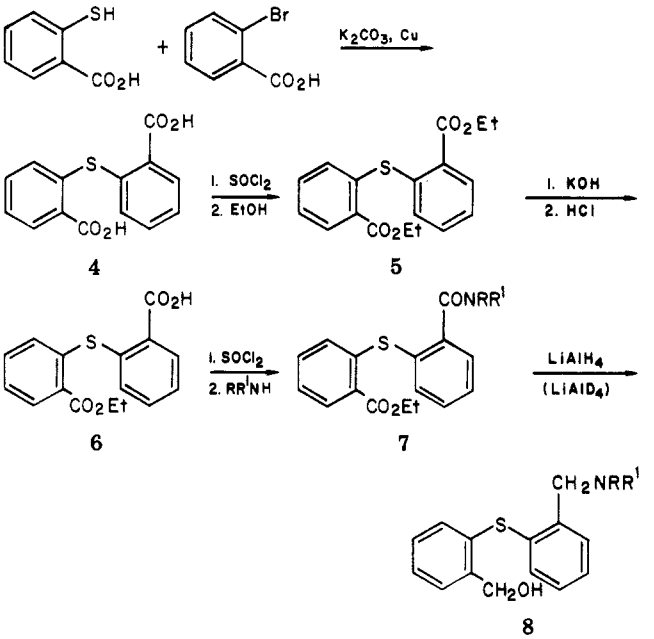
N,N-Dialkyl-6,7-dihydro-5*H*-dibenzo[*b,g*][1,5]thiazocinium salts have been prepared from their corresponding amino alcohols by using *p*-toluenesulfonyl chloride in acetonitrile. The conformational changes of these quaternary salts were studied by NMR and assigned as either TB (twist–boat) or BC (boat–chair). To simplify the assignment of the tetradeuterio derivative 6-benzyl-6,7-dihydro-6-methyl-5*H*-dibenzo[*b,g*][1,5]thiazocinium bromide was prepared. Temperature dependence and concentration/salt effects are discussed.

This paper describes the synthesis and some conformational properties of some *N,N*-dialkyl-6,7-dihydro-5*H*-dibenzo[*b,g*][1,5]thiazocinium salts (**1**). The conformational properties of systems similar to **1** have been described by Renaud and co-workers,[3] who have studied *N*-alkyl-6,7-dihydro-5*H*,12*H*-dibenzo[*c,f*]azocine (**2**) and similar systems by NMR. Also Tanaka and co-workers[4] have studied *N*-alkyl-6,7-dihydro-5*H*-dibenzo[*b,g*][1,5]oxazocines and thiazocines (**3**; X = O, S).



Scheme I[a]



[a] **a**, R = H, R¹ = Me; **b**, R = R¹ = Me; **c**, R,R¹ = -$(CH_2)_4$-; **d**, R,R¹ = -$(CH_2)_5$-; **e**, R = Me, R¹ = $CH_2C_6H_5$; **f**, 5,5,7,7-D_4, R = Me, R¹ = $CH_2C_6H_5$; **g**, 5,5,7,7-D_4, R = CH_3, R¹ = H.

Synthesis

Our previous work[5] has demonstrated the use of *p*-toluenesulfonyl chloride with triethylamine in achieving ring closure of amino alcohols. Scheme I outlines the synthetic route used to prepare the amino alcohols dis-

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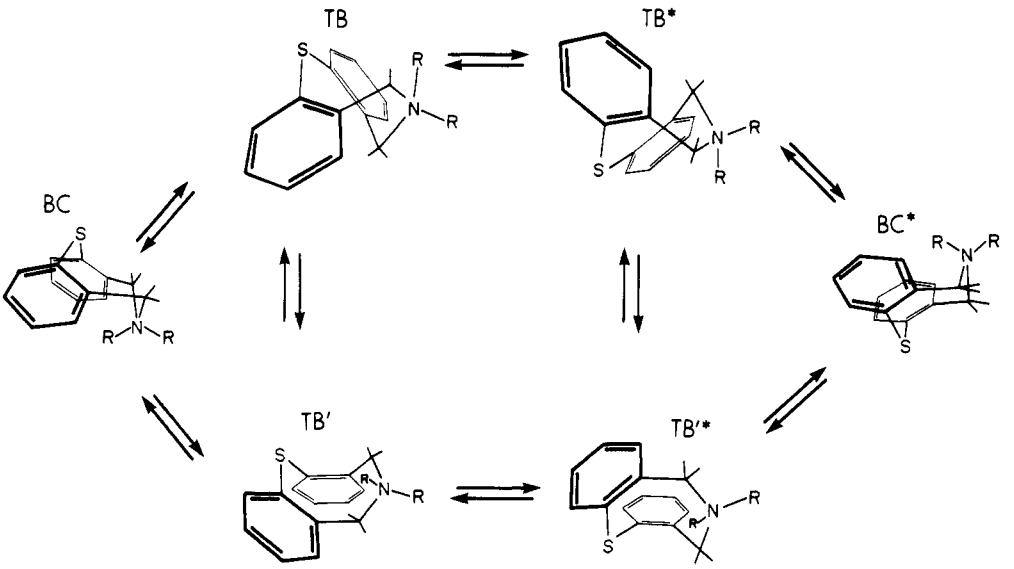
Scheme II

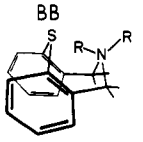


cussed herein. The procedure of Gialdi et al.[6] was modified slightly to give **4** in nearly quantitative yields. The yield of the ester acid **6**, despite varied attempts, never exceeded the stastically expected 50%. The preparation of the amido esters **7** and their reduction to the amino alcohols **8** proceeded without difficulty. Ring closure to the thiazocinium tosylates was achieved at room temperature within 3 h. Even at 0 °C, the reaction was complete within a few hours. Rates of formation of the quaternary salts were monitored by UV. Tanaka and Hashimoto[4b] have reported the synthesis of **1a** by condensing bis[2-(bromomethyl)phenyl] sulfide with methylamine in an autoclave. We have found that this ring formation can also be easily accomplished by treatment of the amino alcohol **8a** with phosphorus tribromide in chloroform at room temperature. Treatment of **1a** with benzyl bromide, in a pressure bottle, afforded the bromide of **1e**. The preparation of **1f** was carried out in the same manner as for **1e** except that the amido ester was reduced with $LiAlD_4$.

^{1}H NMR Spectra

All the quaternary salts exhibited similar NMR properties and undergo similar conformational changes. The nomenclature of Renaud and co-workers[3a] is used here with modifications to describe the possible conformations of this system. From force field calculations on cycloocta-1,4-diene, Allinger and co-workers[7] have concluded that the BC (boat–chair) conformer is significantly more stable than the TB (twist–boat) conformer and estimate that at room temperature the BC should represent about 99% of the equilibrium mixture. In the heteroanalogues studied by Renaud et al.[3] and by Tanaka et al.[4] the TB conformer becomes more important. In the compounds of the present study the TB conformers are present in greater concentrations than their respective BC conformers at ambient temperatures.

Scheme II shows the conformations of these compounds and the conformational exchanges which they undergo. The geometry of the individual conformers has been discussed by Ollis and co-workers.[8] As shown in Scheme II, BC is the boat–chair conformer having C_s symmetry and is described by Renaud et al.[4a] as BC and by Gellatly et al.[8a] as C. The TB conformer is the dissymmetric one described by the above authors as DTB (distorted twist–boat) and boat, respectively. Since we have not done strain-energy calculations for the compounds described in this study, we cannot predict minimum energy twist–boat conformations for them. However, our NMR results indicate that they adopt a dissymmetric twist–boat conformation and that, for compounds **1a–g**, the boat–boat form, BB, is a high-energy transition state. This BB conformer is the one having C_s symmetry and is labeled by Renaud et al.[4a] as BB and by Gellatly et al.[8a] as B. From their strain-energy calculations the latter workers conclude that interconversion of twist–boat forms through a symmetrical boat–boat form "will generally involve relatively low energy barriers". This is not the case for the compounds of this study.



Twisting about the sulfur bonds in a Dreiding model causes an inversion of the TB boat in that the upright boat turns into an upside down boat. This inversion is accomplished in the model with retention of the enantiomeric structure; it is keyed in Scheme II and the discussion by the asterisk (i.e., TB ⇄ TB*). Twisting of the Dreiding model so that the endo group on nitrogen passes across the front of the sulfur atom is keyed by the prime (i.e., TB ⇄ TB′) and does interconvert the enantiomeric structures. It is assumed here, as in the previous papers cited, that the BC conformer does not invert directly to BC* but must pass through the TB forms. The energy barrier for the TB ⇄ BC conversion is high, as noted by the previous authors,[3,4,8] and both BC and TB conformers are detected in the proton NMR spectrum obtained at room temperature of each of the compounds reported in this paper. The coalescence temperature for this exchange is in the range of 110–120 °C, as shown for compound **1c** in Figure 1. Coalescence temperatures for the TB ⇄ TB* and TB ⇄ TB′ exchanges are not easily detected, but the approximate rates of these exchanges can be inferred from the room-temperature spectra of the *N,N*-dimethyl compound (**1b**) and the *N*-methyl-*N*-benzyl compound (**1e**).

(6) Gialdi, F.; Ponci, R.; Baruffin, A. *Farmaco, Ed. Sci.* **1959**, *14*, 648.
(7) Allinger, N. L.; Viskocil, J. F., Jr.; Burkert, U.; Yuh, Y. *Tetrahedron* **1976**, *32*, 33.
(8) (a) Gellatly, R. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1976**, 913. (b) Elhadi, F. E.; Ollis, W. D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 224. (c) Ollis, W. D.; Stoddart, J. F.; Sutherland, I. O. *Tetrahedron* **1974**, *30*, 1903.

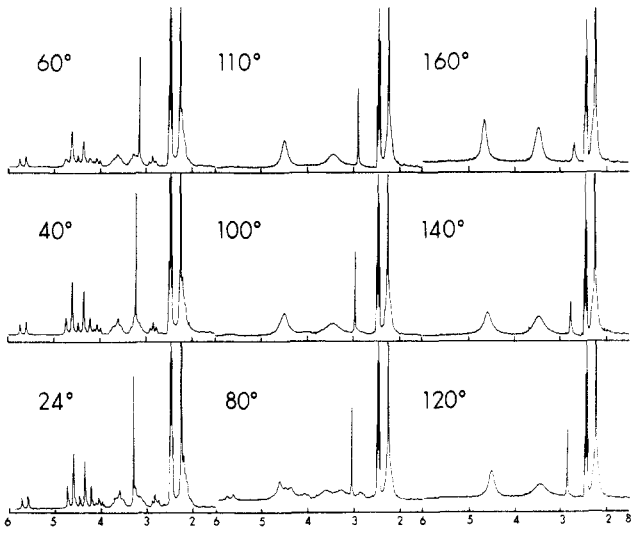


Figure 1. NMR spectra of compound 1c in Me_2SO-d_6 at various temperatures.

Table I. NMR Effects of Various Fast Exchanges

case	conformer	fast exchange	methyl signal	methylene signal
A	BC	none	2 s	1 AB
B1	TB	BC ⇄ TB or TB ⇄ TB* and TB ⇄ TB′	1 s	1 s
B2		TB ⇄ TB′ only (*d*/*l*)	2 s	1 AB
B3		TB ⇄ TB* only (ring inversion)	1 s	1 AB
B4		none	2 s	2 AB

The rigid BC conformer has a plane of symmetry through the N and S atoms, and so the 5- and 7-methylene groups will be isochronous. The ^1H NMR spectrum of the BC conformer of the *N*,*N*-dimethyl compound (**1b**) is expected to display singlets for the *exo*- and *endo*-methyl groups and an AB pattern for the methylenes. If the TB ⇄ TB′ and TB ⇄ TB* exchanges are both fast on the NMR time scale, the spectrum of the TB conformer of compound **1b** should display a methyl singlet and a methylene singlet. This is the case for the bases studied by Renaud et al.[3] and by Tanaka et al.[4] If the TB ⇄ TB′ exchange is fast and the TB ⇄ TB* exchange slow, the resulting TB spectrum will have two methyl singlets and one methylene AB pattern. If the TB ⇄ TB* exchange is fast and the TB ⇄ TB′ exchange slow, the spectrum will show one methyl singlet and one methylene AB pattern. If there is no fast exchange among the four possible TB conformers, the TB spectrum will have two methyl singlets and two AB patterns. The possible cases are shown in Table I.

The spectrum of compound **1b** is shown in Figure 2A (0.1 M in Me_2SO-d_6 at 24 °C). Two stable conformers are apparent in the ratio of 57:43. The major conformer gives one AB system at δ 4.64 and 4.40 with J = 14 Hz and one methyl singlet at δ 3.04. This must represent the TB ⇄ TB* conformers, case B3. The minor form gives one AB system at δ 5.62 and 4.67 with J = 13 Hz and two methyl singlets at δ 2.61 and 3.67. This must represent the BC conformer, case A. The 2.61-ppm peak is assigned to the endocyclic methyl group and the 3.67-ppm peak to the exocyclic methyl on the basis of the aromatic ring shifts expected from measurements on the molecular model.[9]

(9) Bovey, F. A. "Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1969.

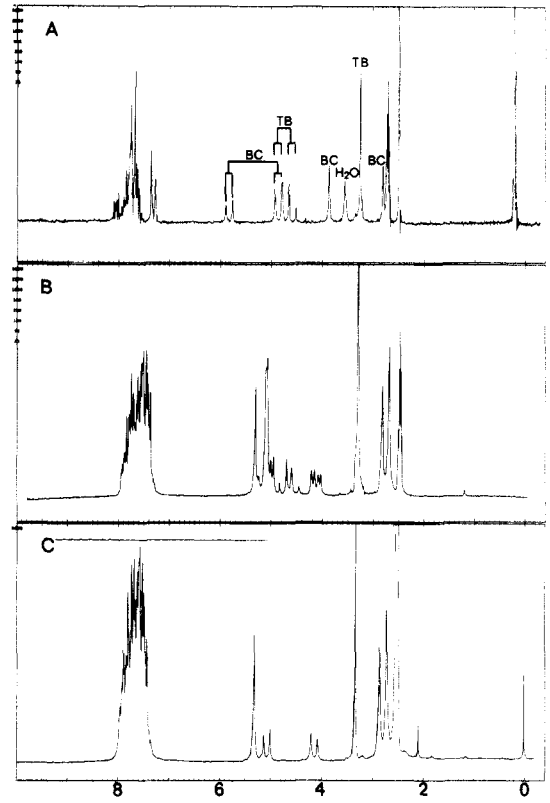


Figure 2. A, compound **1b** tosylate; B, compound **1e** bromide; C, compound **1f** bromide; each ca. 0.1 M in Me_2SO-d_6 at 24 °C.

Table II. Temperature Dependence of Conformer Ratio of 1b Bromide (0.23 M in Me_2SO-d_6)

temp, °C	% BC conformer	temp, °C	% BC conformer
60	35.9	24	44.5
40	38.3		

The TB ⇄ TB′ interconversion evidently has too high an energy barrier to allow rapid interconversion on the NMR time scale at ambient probe temperature (30 °C). Presumably this is because the transition state (BB) involves serious van der Waals repulsion between sulfur and the *N*-alkyl group in the endo position. Previous calculations[7,8] indicate that the rigid BC should be the conformer of lower enthalpy. Thus, the preponderance of the TB conformer at 30 °C indicates that TB is the conformer of higher entropy, as might be expected on the basis of greater mobility. This supposition is supported by the increasing proportion of BC conformer in the equilibrium mixture with decreasing temperature, as shown in Table II.

The spectrum of compound **1e** bromide (0.1 M in Me_2SO-d_6 at 24 °C, Figure 2B) consists of a complex set of lines in the 4.0–5.6-ppm region. To simplify the analysis of this spectrum the 5,5,7,7-tetradeuterio analogue (**1f**) was prepared. The spectrum of this deuterated derivative, recorded under approximately the same conditions, is shown in Figure 2C. Two conformers are apparent. The major one (56%), with a benzylic methylene singlet at 5.29 ppm and a methyl singlet at 2.70 ppm, is assigned as a BC conformer. Only one of the two possible BC conformers (*endo*-methyl and *exo*-methyl) is detected. Because the benzyl group should have a greater steric requirement than the methyl group and because the methyl group has a high-field shift (compare the spectrum of **1b** above), it is assumed to be the *endo*-methyl BC conformer. Only the asymmetric TB conformer (Scheme II) could reasonably be expected to give an AB pattern for the exocyclic benzylic methylene group. The minor conformer (44%) having

Table III. Concentration Dependence of Conformer Ratio of Compound 1d Tosylate in Me_2SO-d_6 at 24 °C

concn, M	% BC conformer	concn, M	% BC conformer
0.005	12.9	0.25	18.4
0.05	14.3		

Table IV. Effect of Added Tetramethylammonium Iodide on the Conformer Ratio of 1b Iodide (0.01 M in Me_2SO-d_6 at 24 °C)

[added salt], M	% BC	[added salt], M	% BC
0	42	0.1	48
0.01	43		

a methyl singlet at 2.84 ppm and an AB pattern at 5.03 and 4.12 ppm (J = 12 Hz) is therefore assigned as the TB conformer. Since a fast TB ⇄ TB′ exchange would lead to isochrony of the exocyclic methylene protons, the exchange must be slow in this case also. If the TB ⇄ TB* exchange were slow and if both conformational states were populated, then two TB methyl signals would be detected. Since only one such methyl resonance is detected in the spectrum of **1f** (Figure 2C), the exchange is fast or the equilibrium is very one-sided. The shift of the TB methyl group in **1f** is at significantly higher field ($\Delta\delta$ = 0.20 ppm) than that of the averaged TB methyl group of **1b** (Figure 2A). Thus, independent of the TB ⇄ TB* interconversion rate, the TB ring conformer of **1f** must exist mainly in the *endo*-methyl form.

For all these compounds, changes in the concentration of compound or of added salt will change the relative amounts of BC and TB conformers and the shift values of the 5- and 7-methylene groups. Increasing concentrations of compound (Table III) or of added salt ($Me_4N^+I^-$, Table IV) result in an increasing stability of the BC relative to TB conformer. This relative increase in stability of the BC form may be due to an entropy loss in the TB form, caused by intermolecular electrostatic interactions.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Microanalyses were performed by Atlantic Microlab, Galbraith Laboratories, and the Analytical Department of Burroughs Wellcome. All C, H, and N analyses are within ±0.4%. UV spectra were recorded with a Beckman DB spectrophotometer; NMR spectra were measured with a Varian XL-100-15 spectrometer. Chemical shifts are reported in parts per million downfield from Me_4Si. Molecular weight determinations (vapor-phase osmometry) were performed by Galbraith Laboratories. Physical data are given in Table V.

2,2′-Dicarboxydiphenyl Sulfide (4). 2-Bromobenzoic acid (40.0 g, 0.20 mol) and 2-mercaptobenzoic acid (32.0 g, 0.20 mol) were dissolved in 140 mL of water containing 56.0 g (0.40 mol) of potassium carbonate. Powdered copper (13.0 g, 0.20 mol) was added, and the reactants were heated in a bomb at 130–140 °C for 3 h. When the mixture cooled, the filtrate was acidified with concentrated HCl to give 52.8 g of the diacid **4**, mp 225–230 °C (lit.[3] mp 233 °C).

2,2′-Dicarbethoxydiphenyl Sulfide (5). Diacid **4** (54.8 g, 0.20 mol) was treated with excess thionyl chloride (100 mL) at 60 °C for 5 h. Removal of excess thionyl chloride and then boiling with 200 mL of absolute EtOH for 0.5 h gave 62.0 g (90%) of the diester **5** (from EtOH/water), mp 56–57 °C (lit.[3] mp 58–59 °C).

2-Carbethoxy-2′-carboxydiphenyl Sulfide (6). Diester **5** (120.0 g, 0.40 mol) was added to a solution of KOH (26.4 g, 0.40 mol) in 1 L of EtOH and stirred at ambient temperature for 4 days. Acidification with concentrated HCl followed by concentration and extraction with dilute $NaHCO_3$ gave a brown solid. Trituration with warm benzene gave 43.0 g (37%) of the ester acid **6**, mp 122–123 °C.

2-Carbethoxy-2′-(pyrrolidinocarbonyl)diphenyl Sulfide (7c). Treatment of **6** (20.0 g, 0.066 mol) with excess thionyl chloride gave 20.1 g of the acid chloride, which was then dissolved in 150 mL of acetonitrile and added to a solution of pyrrolidine (4.8 g, 0.066 mol) in 50 mL of triethylamine. After 3 h of stirring at room temperature, the reaction mixture was concentrated in vacuo, dissolved in 250 mL of chloroform, and extracted with dilute aqueous HCl and dilute $NaHCO_3$. The organic layer was dried (Na_2SO_4) to yield 23.3 g (98%) of the amido ester **7c**, mp 117–119 °C (acetone–hexane).

2-Carbethoxy-2′-(piperidinocarbonyl)diphenyl Sulfide (7d). By use of the same procedure as described for **7c**, **7d** was obtained in a yield of 75% as a white solid after recrystallization from acetone/*n*-hexane; mp 111–113 °C.

2-Carbethoxy-2′-[(dimethylamino)carbonyl]diphenyl Sulfide (7b). A solution of the acid chloride (32.0 g, 0.10 mol) of **6** in 150 mL of dry dioxane was added, with cooling, to 100 mL of a 25% aqueous solution of dimethylamine in 150 mL of dioxane. After 1 h, the reaction mixture was acidified with concentrated HCl and filtered. The filtrate was removed and worked up as described for **7c** to give a 32.0 g (97%) of an orange oil. Upon trituration of this oil with ether/petroleum ether there was isolated 27.0 g of a tan solid, **7b**, mp 78–81 °C.

2-Carbethoxy-2′-[(methylamino)carbonyl]diphenyl Sulfide (7a). Prepared as described for **7b**, this compound was

Table V. Physical Properties

compd	yield, %	mp, °C	crystn solv	formula[d]	UV λ, nm[i]
4[a]	96	225-230			
5[b]	90	56-57			
6	37	122-123	c	$C_{16}H_{14}O_4S$	
7a	96	94-96	EtOH-H_2O	$C_{17}H_{17}NO_3S$	
7b	97	78-81	Et_2O-petroleum ether	$C_{18}H_{19}NO_3S$	
7c	72	117-119	acetone-hexane	$C_{20}H_{21}NO_3S$	
7d	75	111-113	acetone-hexane	$C_{21}H_{23}NO_3S$	
8a	90	216-219	EtOH-EtOAc	$C_{15}H_{17}NOS\cdot HCl$	
8b	60	162-164	EtOH-Et_2O	$C_{16}H_{19}NOS\cdot HCl$	
8c	93	190-192	EtOH-H_2O	$C_{18}H_{21}NOS\cdot HCl$	
8d	60	172-173	MeOH-acetone	$C_{19}H_{23}NOS\cdot HCl$	
9	86	oil		$C_{15}H_{13}D_4NOS$	
1a	85	217-219	EtOH-acetone	$C_{15}H_{15}NS\cdot HCl$	230, 252, 278, 304 sh
1b	30	125-126	H_2O	$C_{23}H_{25}NO_3S_2\cdot H_2O$[e]	228, 254, 276, 312
1c	71	210-213	EtOH-acetone	$C_{25}H_{27}NO_3S_2$[f]	224, 254, 276, 310
1d	45	238-240	EtOH-acetone	$C_{26}H_{27}NO_3S_2$[g]	224, 254, 276, 310
1e	56	196-199	MeOH	$C_{22}H_{22}BrNS$	226, 254, 276, 312
1f	65	198-198.5	MeOH	$C_{22}H_{18}D_4BrNS$	226, 252, 273, 310
1g	32	oil		$C_{15}H_{11}D_4NS$[h]	

[a] Lit.[4] mp 233 °C. [b] Lit.[4] mp 58–59 °C. [c] Triturated with benzene. [d] All C, H, and N analysis were within ±0.4%. [e] H_2O analysis was within 6%. [f] Molecular weight determination (vapor-phase osmometry) was within 5.8%. [g] Molecular weight determination was within 2%. [h] UV, TLC, and NMR were consistent with the proposed structure. [i] In 95% EtOH.

isolated as a tan solid: 96% yield; mp 94–96 °C (ethanol–H_2O).

2-(Hydroxymethyl)-2′-(pyrrolidinomethyl)diphenyl Sulfide (8c). To a slurry of 13.3 g (0.35 mol) of $LiAlH_4$ in 800 mL of THF was added a solution of 25.0 g (0.07 mol) of **7** in 150 mL of THF. Stirring at room temperature overnight, adding water followed by dilute NaOH, filtering, and concentrating gave a yellow oil. Dissolution in ether followed by treatment with ethereal HCl produced 17.0 g (93%) of the hydrochloride salt **8c**, mp 190–192 °C (ethanol–H_2O).

2-(Hydroxymethyl)-2′-(piperidinomethyl)diphenyl Sulfide (8d). Reduction of **7d** with $LiAlH_4$ yielded a white solid (60%) as the hydrochloride salt, mp 172–173 °C (MeOH–acetone).

2-[(Dimethylamino)methyl]-2′-(hydroxymethyl)diphenyl Sulfide (8b). As for **8c**, the hydrochloride salt was isolated in a yield of 60%; mp 162–164 °C (ethanol–ether).

2-(Hydroxymethyl)-2′-[(methylamino)methyl]diphenyl Sulfide (8a). Prepared as described for **8c**, this compound was isolated as the hydrochloride salt: 90% yield; mp 216–219 °C (ethanol–ethyl acetate).

2-[[2-[(Methylamino)methyl-d_2]phenyl]thio]benzyl-α-α-d_2 Alcohol (9). The amido ester **7a** was reduced with $LiAlD_4$, as described above, to furnish 5.0 g of an orange oil (86%). ^1H NMR revealed no methylene proton absorptions. The compound was used without further purification.

Spiro[5*H*,7*H*-dibenzo[*b*,*g*][1,5]thiazocinetetramethyleneammonium] Tosylate (1c). A solution of 9.0 g (0.047 mol) of *p*-toluenesulfonyl chloride in 50 mL of dry CH_3CN was added to 13.0 g (0.043 mol) of **8c** in 75 mL of dry CH_3CN and 25 mL dry triethylamine. After being stirred at room temperature for 18 h, the solution was filtered and concentrated in vacuo. The residue was triturated with dry acetone and subjected to high vacuum to remove any Et_3N·HCl. Recrystallization from EtOH/acetone afforded 13.9 g (71%) of a white solid, **1c**: mp 210–213 °C; UV (95% EtOH) 224, 254, 276, 310 nm; mol wt 480 (5.8% error).

Spiro[5*H*,7*H*-dibenzo[*b*,*g*][1,5]thiazocinepentamethyleneammonium] Tosylate (1d). Ring closure was effected for **8d** in the same manner as for **1c**. Recrystallization from EtOH/acetone gave the azaspiro compound **1d**: 45% yield; mp 238–240 °C; UV (95% EtOH) 224, 254, 276, 310 nm; mol wt 458 (±2% error).

***N*,*N*-Dimethyl-5*H*,7*H*-dibenzo[*b*,*g*][1,5]thiazocinium Tosylate (1b).** The crude reaction product was obtained as described for **1c**. Attempts to remove triethylamine hydrochloride by high-vacuum sublimation resulted in decomposition. Recrystallization from water afforded the desired compound, **1b**: 30% yield; mp 125–126 °C; UV (95% EtOH) 228, 254, 276, 312 nm.

6,7-Dihydro-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocine (1a). Phosphorus tribromide (13.5 g, 0.05 mol) in 100 mL of chloroform was added to an ice-cooled solution of 19.6 g (0.076 mol) of **8a** in 1 L of chloroform, which was kept at ice-bath temperature for 2 h and then at room temperature for 17 h. The solution was refluxed for 2 h, cooled, diluted with 500 mL of water, and made basic with solid K_2CO_3. The organic layer was separated, dried (K_2CO_3), and concentrated in vacuo to give a yellow oil. Trituration with ether, followed by ethereal HCl, gave the hydrochloride salt **1a**: 85% yield; mp 217–219 °C (ethanol–acetone); UV (95% EtOH) 230, 252, 278, 304 (sh) nm.

6,7-Dihydro-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocine-*5*,*5*,*7*,*7*-d_4 (1g). The procedure described for **1a** was followed; it yielded the base in 32% yield as an oil. The UV, TLC, and NMR were compatible with the desired ring system.

6-Benzyl-6,7-dihydro-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocinium Bromide (1e). Benzyl bromide (3.4 g, 0.02 mol) was mixed with 2.3 g (0.0096 mol) of **1a** in a pressure bottle and was left to stand at 60 °C for 3 days. Dilution with ether yielded a white solid, **1e**: 56% yield; mp 196–199 °C (MeOH); UV 95% (EtOH) 226, 254, 276, 312 nm.

6-Benzyl-6,7-dihydro-6-methyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocinium-*5*,*5*,*7*,*7*-d_4 Bromide (1f). The same procedure as for **1e** was followed with **1g** and benzyl bromide to give a white solid: 65% yield; mp 198–198.5 °C. The UV, TLC, and NMR were compatible with the desired structure.

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Registry No. 1a, 32636-23-0; **1b**, 76583-89-6; **1b** bromide, 76583-90-9; **1b** iodide, 76583-91-0; **1c**, 76583-93-2; **1d**, 76583-95-4; **1e**, 76599-28-5; **1f**, 76583-96-5; **1g**, 76583-97-6; **4**, 22219-02-9; **5**, 62220-51-3; **6**, 62220-52-4; **6** acid chloride, 62220-53-5; **7a**, 62220-56-8; **7b**, 62220-54-6; **7c**, 62220-62-6; **7d**, 62220-63-7; **8a**, 62220-59-1; **8b**, 62763-91-1; **8c**, 62220-64-8; **8d**, 62763-92-2; **9**, 76583-98-7; $MeNH_2$, 74-89-5; Me_2NH, 124-40-3; pyrrolidine, 123-75-1; piperidine, 110-89-4; 2-bromobenzoic acid, 88-65-3; 2-mercaptobenzoic acid, 147-93-3; benzyl bromide, 100-39-0; $Me_4N^+I^-$, 75-58-1.