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Synthesis and Conformational Dynamics of 1,1′,5,5′-Tetrahydro-7,7′,8,8′-tetramethyl-3,3′-spirobi[2,4-benzodithiepin]

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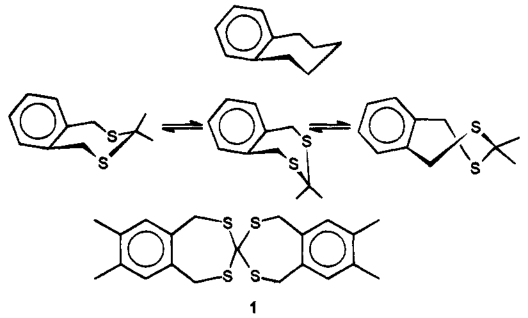
The title compound **1** was prepared in one step from 1,2-bis(chloromethyl)-4,5-dimethylbenzene and sodium trithiocarbonate generated *in situ* from carbon disulfide, hydrogen sulfide, and sodium ethoxide in ethanol. Conformational analysis of **1** has been carried out using ^{1}H- and ^{13}C-NMR spectroscopy, X-ray analysis, and semiempirical calculations. The results indicate that in the solid state **1** exists in a chair–twist-boat conformation while in solution it undergoes two intramolecular dynamic processes, pseudorotation at lower temperature (~250 K) and ring inversion at higher temperature (~280 K), with the activation energies ($\Delta G^{\ddagger}$) of approximately 54 and 56 kJ/mol, respectively.

Introduction

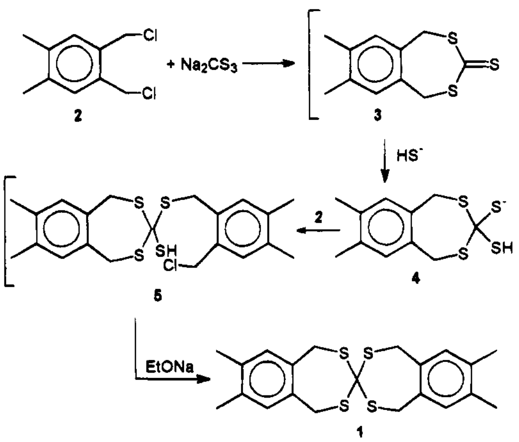
The conformational analysis of seven-membered and large ring compounds is not straightforward because these compounds are flexible with many conformational possibilities.[1] Analysis of the conformational behavior of such compounds is still a challenging problem. The situation becomes even more complicated when heteroatoms such as oxygen, sulfur, or nitrogen are present in a ring. For example, in contrast to benzocycloheptene, which adopts a chair conformation,[2] 2,4-benzodithiepin derivatives exist as a mixture of chair, boat, and/or flexible twist forms.[3–5] Very recently, a detailed analysis of Raman spectra of 3,3-dimethyl-2,4-benzodithiepin indicated that it exists in the crystal, liquid, and solution states in three conformations in equilibrium (Chart 1).[6,7]

In connection with our studies on the anomeric effect in the cyclic 1,3-dithia systems[8,9] we became interested in the conformation of spirobenzodithiepin derivatives. A few of these compounds have been previously studied in connection with the so-called spiroconjugation and its effect on UV and ^{13}C-NMR spectra.[10,11] The characteristic spectral changes due to spiroconjugation in heterospirans are often different from those of spirocarbons and are interpreted mainly in terms of the through-bond $n \rightarrow \sigma^*$ interaction. However, to the best of our knowledge, structural and conformational properties of spirobenzodithiepins have not been investigated. This prompted us to investigate the synthesis and conformational behavior of 1,1′,5,5′-tetrahydro-7,7′8,8′-tetramethyl-3,3′-spirobi[2,4-benzodithiepin] (**1**) using a combination of NMR spectroscopy, quantum-chemical calculations, and X-ray analysis. The results of these studies are reported herein.

Chart 1



Scheme 1



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0022-3263/95/1960-6335$09.00/0

Table 1. Selected Bond Distances (Å)

atom 1	atom 2	distance[a]	atom 1	atom 2	distance[a]
S1	C1	1.823(5)	S4	C1	1.821(4)
S1	C2	1.815(5)	S4	C5	1.811(5)
S2	C1	1.818(5)	C2	C6	1.502(7)
S2	C3	1.822(4)	C3	C7	1.515(7)
S3	C1	1.822(5)	C4	C14	1.508(6)
S3	C4	1.814(4)	C5	C15	1.515(7)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2. Selected Bond Angles (deg)[a]

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
C1	S1	C2	102.5(3)	S2	C3	C7	114.4(4)
C1	S2	C3	103.9(2)	S3	C4	C14	113.3(3)
C1	S3	C4	99.5(3)	S4	C5	C15	118.1(3)
C1	S4	C5	102.2(3)	C2	C6	C7	121.9(4)
S1	C1	S2	115.5(3)	C2	C6	C11	119.2(4)
S1	C1	S3	113.2(3)	C3	C7	C6	122.3(4)
S1	C1	S4	101.1(3)	C3	C7	C8	119.1(4)
S2	C1	S3	107.7(2)	C4	C14	C15	123.3(4)
S2	C1	S4	106.3(2)	C4	C14	C19	118.3(5)
S3	C1	S4	112.9(2)	C5	C15	C14	125.3(4)
S1	C2	C6	116.2(3)	C5	C15	C16	116.7(5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Results and Discussion

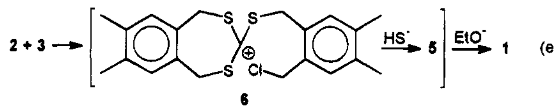
Synthesis of Tetrathiospiran 1. The title compound **1** was obtained by treatment of 1,2-bis(chloromethyl)-4,5-dimethylbenzene (**2**) with a solution of sodium trithiocarbonate that was generated *in situ* from carbon disulfide, hydrogen sulfide, and sodium ethoxide in ethanol.[12] It is a crystalline compound having mp 255–258 °C. High resolution mass spectra and satisfactory elemental analysis helped to confirm the structure of **1** as 1,1′,5,5′-tetrahydro-7,7′8,8′-tetramethyl-3,3′-spirobi[2,4-benzodithiepin]. First of all, the HRMS spectrum showed a molecular peak at 404.0765 corresponding to the formula $C_{21}H_{24}S_4$. In the electron impact mass spectrum at 70 eV, in addition to the molecular ion at *m*/*z* 404.1 (10.5%), four intense fragment peaks occurred at *m*/*z* 241.0 (41.1%), 163.0 (base peak), 132.1 (64.5%), and 117.1 (19.3%). The first two are due to fragmentation of **1** into the monocyclic trithiocarbonate and 3,4-dimethylbenzotetrahydrothiophenium ions. The ^{1}H- and ^{13}C-NMR spectra are also in accord with the proposed structure of **1**. However, since this compound exists in a conformational equilibrium, the spectra will be discussed later in connection with a solution conformation of **1**.

Although the mechanism of the formation of **1** was not investigated in detail, the first reaction stage between **2** and sodium trithiocarbonate results most probably in the formation of the monocyclic trithiocarbonate **3** which was, as a matter of fact, the expected reaction product. However, **3** reacts further with hydrogen mercaptide present in a reaction mixture to give the mercapto anion **4**. This undergoes, in turn, alkylation by the second molecule of **2** which leads to the corresponding alkylated product **5**. Under alkaline conditions the reaction is terminated by cyclization and affords the spiro compound **1** (Scheme 1).

Table 3. Selected Results of AM1 and PM3 Calculations of Various Conformations of 1

	AM1			PM3		
conformation of 1	H_f (kcal)	relative total energy (kcal)	μ (D)	H_f (kcal)	relative total energy (kcal)	μ (D)
chair–chair, **A**	36.37	0	1.54	53.17	0	3.22
chair–twist-boat, **B**	36.99	0.2	1.70	53.06	2.4	2.57
chair–boat, **C**	41.34	0.6	1.92	53.42	2.9	3.46
boat–boat, **D**	113.14	17.8	3.47	56.23	5.3	3.67
twist boat–twist-boat, **E**	289.92	6.6	1.31	56.29	5.4	0.32

An alternative pathway for the formation of **1** in the reaction under discussion may also be proposed which involves alkylation of the thiocarbonyl sulfur in the transiently formed **3** by **2** to give a highly stabilized carbocation **6**. It should be quickly trapped by hydrogen mercaptide present in the reaction mixture to give **5** which undergoes cyclization to **1**.



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(eq. 1)

Crystal and Molecular Structure of 1. To confirm the proposed structure for **1** and to get better insight into the solid state conformation of this interesting spiro molecule we decided to determine its crystal and molecular structure by X-ray diffractometric technique. The suitable crystals of **1** for X-ray analysis were obtained by slow crystallization from a benzene solution. The structure has been solved by direct methods and refined by full-matrix least-squares technique to the final value $R = 0.042$. A three-dimensional view of the molecule of **1** and the atom numbering system are shown in Figure 1. Figure 2 shows the packing of the molecules of **1** in unit cell. Table 1 contains selected bond distances. In Table 2 selected angles are given.

As is seen from Figure 1, the molecule of **1** consists, indeed, of four condensed rings, i.e., two six-membered benzene rings and two seven-membered dithiepin rings coupled together by the spiro-carbon atom. More interestingly, analysis of the crystal structure of **1** revealed that two seven-membered rings have different conformations as indicated by the signs and values of the corresponding torsional angles. The first seven-membered ring (C1–S1–S2–C2–C3–C6–C7) has a symmetry plane passing through the spiro-carbon atom C1 and the C6–C7 bond, and therefore, it exists in a chair conformation. The second seven-membered ring (C1–S3–S4–C4–C5–C14–C15) has a 2-fold axis of symmetry passing through the spiro-carbon atom C1 and the C14–C15 bond which means it has a twist-boat conformation. In the latter more deformed conformation, the valence angles are more differentiated than those in the more symmetrical chair-ring (see below).

C1–S2–C3 = 103.9(2)°
C1–S1–C2 = 102.5(3)°
S2–C3–C7 = 114.4(4)°
S1–C2–C6 = 116.2(3)°

C1–S3–C4 = 99.5(3)°
C1–S4–C5 = 102.2(3)°
S3–C4–C14 = 113.6(3)°
S4–C5–C15 = 118.1(3)°

As a result of the ring fusion, the benzene rings are slightly deformed along the C8–C11 and C16–C19 axes; this is reflected in a small increase of the corresponding valence angles [123.1(5)°, 122.5(5)° and 123.2(4)°, 123.6-

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[12] In the preparation of 1,3-dithiane-3-thione from sodium hydrogen sulfide, carbon disulfide, and 1,3-dibromopropane the corresponding tetrathiospiran was formed as a byproduct in a very low yield: Jonston, T. P.; Stringfellow C. R., Jr.; Gallagher, A. *J. Org. Chem.* **1962**, *27*, 4068; see also ref 10.

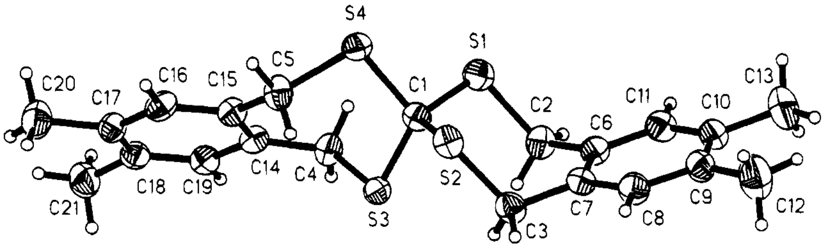

Figure 1. ORTEP view of the molecular structure of **1** with the atom numbering system.

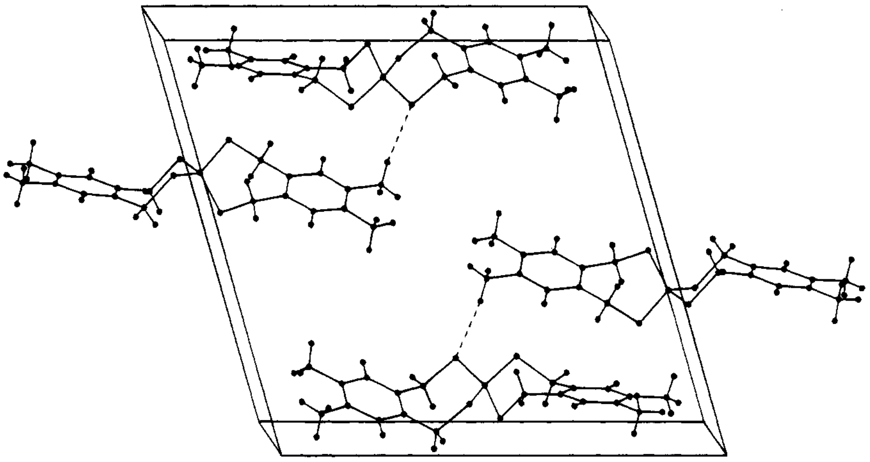

Figure 2. Molecular packing of **1** in crystal. The dotted lines indicate the short intermolecular H···S contacts (2.917A).

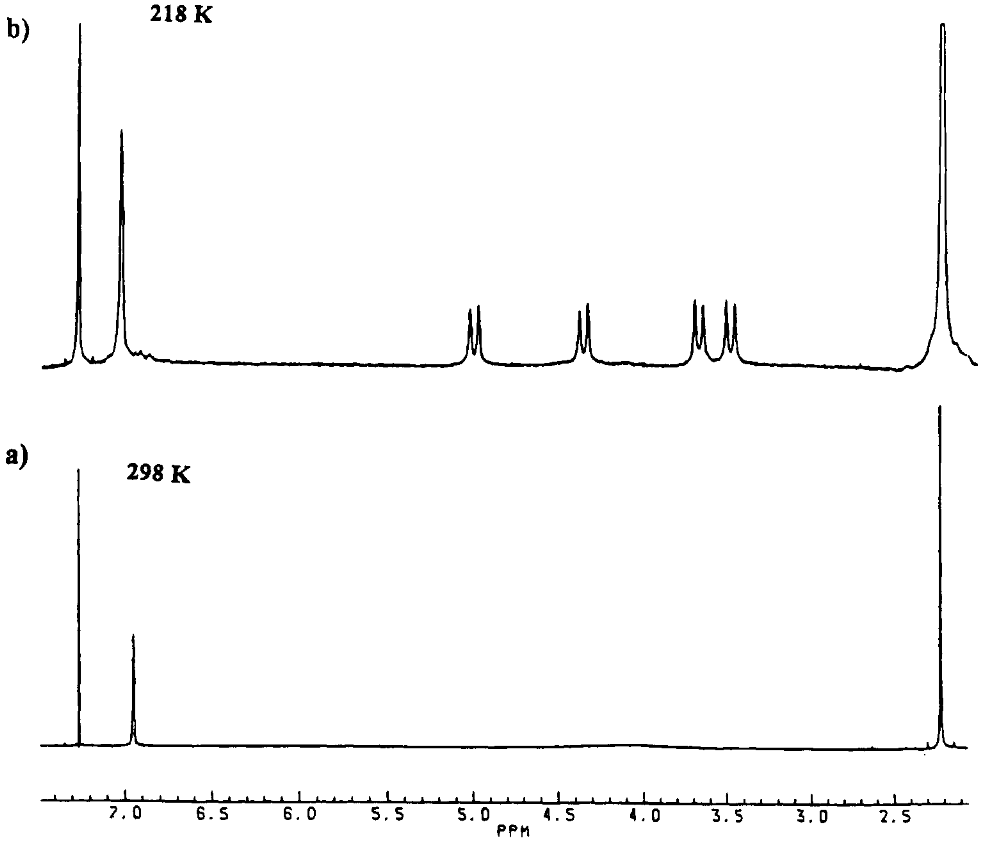

Figure 3. 300 MHz ^{1}H-NMR spectra of the spiro-compound **1** recorded at 218 and 298 K.

(4)°]. Since it is attached to conformationally different seven-membered rings, the benzene ring planes form an angle of 50.3(2)°. Moreover, whereas the benzene ring C6−C11 is situated almost parallel to the C1−S1−S2 plane [2.7(3)°], the angle between the second benzene ring C14−C19 and the C1−S1−S4 plane is 44.9(2)°.

The spiro-junction of two seven-membered rings is almost symmetrical as evidenced by the angle of 93.6-

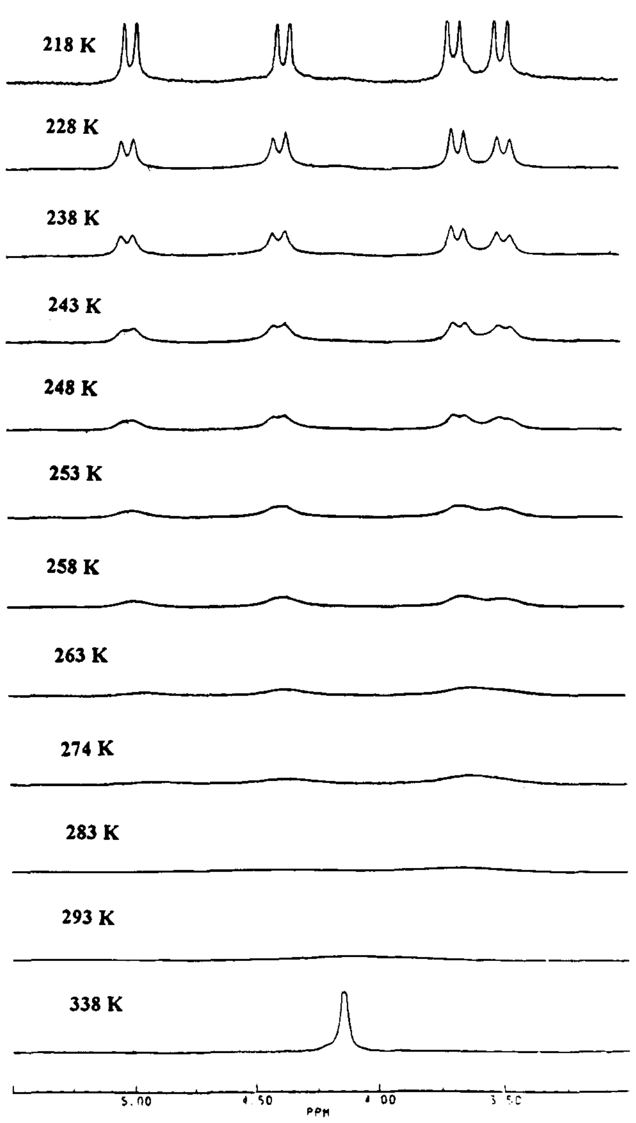

Figure 4. Variable temperature 300 MHz ^{1}H-NMR spectra of the spiro-compound **1** recorded in the temperature range from 218 to 338 K. Only expanded spectra of the methylene protons are shown.

(2)° between the C1−S1−S2 and C1−S3−S4 planes. The bond distances between the spiro-carbon atom C1 and four sulfur atoms are the same. However, nonbonding distances between sulfurs are different [S1⋯S4 = 2.815(5) Å, S1⋯S3 = 3.042(5) Å, S2⋯S3 = 2.938(5) Å, S2⋯S4 = 2.911(5) Å].

The sulfur−carbon and carbon−carbon bond lengths have standard values and are in good agreement with the literature data.

Semiempirical Calculations. In contrast to the solid state, in a solution the tetrathiospiran **1** can theoretically adopt a large number of conformations. However, only a few conformers are stable enough to contribute to the conformational equilibrium. To gain a better insight into the conformational properties of **1**, five conformations, chair−chair (**A**), chair−twist-boat (**B**), chair−boat (**C**), boat−boat (**D**), and twist-boat−twist-boat (**E**), were selected for semiempirical calculations. In the first instance, these five conformations were optimized by means of molecular mechanics calculations (MM2), and the geometrical parameters obtained by this method were used as preliminary data for further SCF calculations. Two semiempirical methods AM1 and PM3 were employed. The first of them was selected because modification of the core repulsion function yields improvement over the MNDO method in treatment of crowded molecules.[13] The second was chosen because its parameter sets predict more reliable geometries for molecules containing third-row elements such as sulfur.[14] The geometry of each conformer was optimized with respect to all structural parameters (bond lengths, valence, and torsional angles). The calculated relative total energies, heats of formation, and dipole moments are collected in Table 3.

Table 4. Crystal Data and Experimental Details

molec formula	$C_{21}H_{24}S_4$
molec wt	404.08
crystallizn solvent	benzene
crystallogr syst	monoclinic
space grp	$P2_1/n$
a (Å)	17.962(3)
b (Å)	6.364(2)
c (Å)	18.254(2)
β (deg)	107.24(1)
Z	4
V (Å^3)	1993(1)
μ (cm^{-1})	4.60
D_x (g/cm^3)	1.349
cryst. dimens. (mm)	0.05, 0.1, 0.3
maximum 2θ (deg)	50
radiatn, λ (Å)	Mo Kα, 0.7107
scan mode	$\omega/2\theta$
scan width	$0.85 + 0.35 \tan\theta$
hkl ranges	$h = 0, 21$ $k = 0, 7$ $l = -21, 21$
no. of reflns measured	3991 total 2134 $I \geq 3\sigma(I)$
no. of params	226
R	0.042
max shift/esd	0.01

The stability of the conformers **A**−**C** is comparable. The chair−twist-boat form **B**, which was found in the solid state, seems to be slightly less favorable [by 0.2 kcal (AM1), 2.4 kcal (PM3)] than the chair−chair conformer **A**. Semiempirical methods based on MNDO obviously underestimate rotational barriers. However, it can be stated that the transformation to the conformation **B** can occur by pseudorotation since it requires little energy.[15] The ring inversion from boat to chair requires a higher energy because it involves stronger deformations of valence angles at the sulfur atoms (from 103−106° to 112−117° found in the boat conformation).

The AM1 method understimates the carbon−sulfur bond lengths (1.73−1.78 Å) whereas the values predicted by PM3 (1.82−1.83 Å) are close to those obtained from X-ray study.

Net charges at sulfur atoms are positive, and the central spiro-carbon atom has a negative charge of [−0.5 (AM1), −0.3 (PM3)]. The results of calculations by both methods reflect a general tendency that with longer C−S bonds and larger C−S−C valence angles the sulfur atoms become less positively charged. However, in the sterically crowded boat−boat conformation **D** positive charge at sulfur increases slightly with the increased bond length.

The core−core repulsion energies increase in the following order: **E** < **B** ≤ **A** < **C** < **D**, thus confirming

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[13] Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[14] Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 202.

[15] The value of 2 kcal/mol has been calculated for unsaturated seven-membered rings: Friebolin, H.; Kabuss, S. In *NMR in Chemistry*; Pesse, B., Ed.; Academic Press: New York, 1965, p 125.

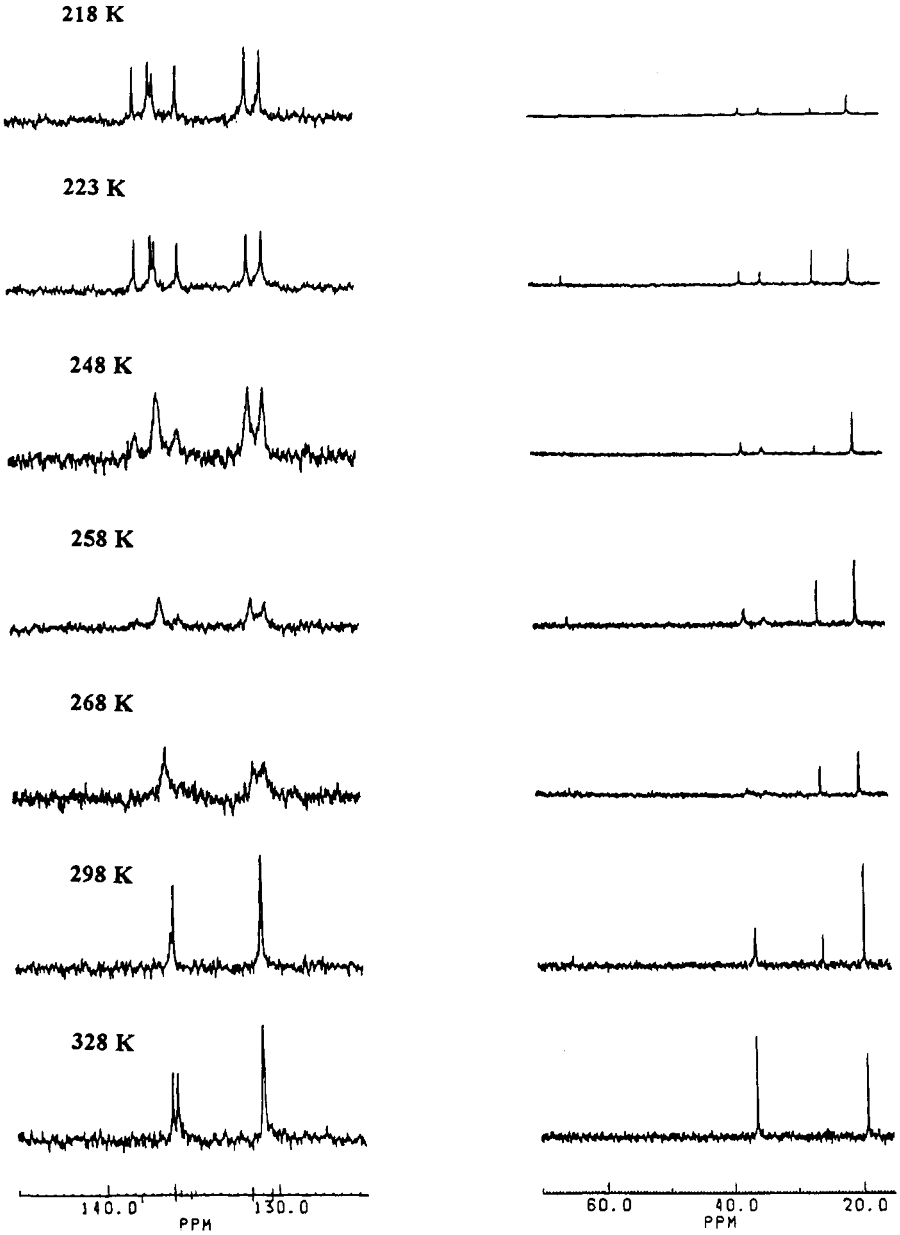

Figure 5. Variable temperature 75.468 MHz ^{13}C-NMR spectra of the spiro-compound **1** recorded in the temperature range from 218 to 328 K. The aromatic and aliphatic regions are shown separately.

that the instability of the conformation **D** results from steric hindrance that can be released by twisting the ring.

NMR Studies of Tetrathiospiran 1. Figure 3a displays the ^{1}H NMR spectrum of the spiro-compound **1** recorded at room temperature. The spectrum shows only a sharp signal at $\delta = 2.21$ ppm corresponding to the methyl group protons attached to the phenyl ring and a signal at $\delta = 6.95$ ppm due to aromatic protons. In the region of the methylene protons at 3–5 ppm only a very broad line is observed. Such a spectrum is typical for compounds which undergo fast and/or intermediate dynamic processes on the NMR time scale.

By making use of the NMR techniques, several research groups have investigated the dynamics of seven-membered rings.[1] In contrast, little attention has been paid to seven-membered spiro compounds. It has been found that pseudorotation in the seven-membered ring systems covers an extremely wide range of energy barriers.[16] As shown by Friebolin and co-workers for a series of 2,4-benzodithiepin derivatives, the barriers to pseudorotation for seven-membered rings containing two sulfur atoms are rather low.[17–19] The recent results of Klimovitskii et al.[5] are consistent with previous data.

Figure 3b shows the ^{1}H NMR spectrum of the compound **1** recorded at 218 K. On the basis of this low temperature experiment the methylene proton resonances can be easily assigned. The observed four doublets with very different chemical shifts suggest a different conformation in a solution for both rings of the spiro system investigated. As seen from NMR studies for the spiro compound **1**, when both phenyl rings are in perpendicular planes, the C_s symmetry is apparent.

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(16) Anet, F. A. L.; Anet, R. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, San Francisco, London, 1975; p 543.

(17) Schmid, H. G.; Friebolin, H.; Kabuss, S.; Mecke, R. *Spectrochim. Acta* **1966**, *22*, 623.

(18) Kabuss, S.; Lüttringhaus, A.; Friebolin, H.; Mecke, R. *Z. Naturforsch.* **1966**, *B21*, 320.

(19) Friebolin, H. In *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH: Weinheim, 1991; p 263.

Furthermore, this conclusion is consistent with our X-ray data which revealed that in the solid state the title compound **1** crystallizes with one molecule as independent unit and with chair and twist-boat geometry for both benzodithiepin rings. According to the data published elsewhere, the resonances found at $\delta = 3.46$ ppm and $\delta = 3.65$ ppm correspond to the methylene protons of a chair conformation,[18] whereas the downfield signals at $\delta = 4.37$ ppm and $\delta = 5.00$ ppm are from protons in boat or twist-boat geometry of the latter ring. In both cases the geminal axial–equatorial coupling constants are 15.26 Hz.

In order to study the nature of the dynamic process in detail, a series of variable temperature experiments in the temperature range from 218 to 338 K were carried out. The expanded part of the methylene region is shown in Figure 4. When the sample is cooled to 218 K, the freezing of the intramolecular dynamics is observed and geminally paired protons are very well resolved. With an increase in temperature the coalescence temperature T_c of pseudorotation can be established. It is interesting to point out that for both benzodithiepin rings the T_c values were found to be slightly different. At 300 MHz for proton nucleus, T_c for twist-boat geometry is 248 K whereas for a chair conformation it is 253 K. From the Eyring equation, the calculated free enthalpies of activation $\Delta G^{\ddagger}$ are 53.09 and 54.20 kJ/mol for twist-boat and chair conformations, respectively. It is noteworthy that one observes a very small difference in $\Delta G^{\ddagger}$ parameters (1.1 kJ/mol) for both conformations.

For ring inversion the coalescence temperature is 280 K. The appropriate $\Delta G^{\ddagger}$ parameters are 56.15 and 56.73 kJ/mol for both rings. In the temperature range from 258 to 298 K only very broad signals of the methylene protons are monitored. At higher temperature (338 K), owing to very fast ring inversion, only one average signal of the methylene protons at $\delta = 4.29$ is observed. The results shown here are in agreement with the data published elsewhere[16] for other 2,4-benzodithiepin derivatives and further confirmed the very low pseudorotation barrier and conformational mobility of the seven-membered ring systems containing two sulfur atoms.

Further results regarding the dynamics of the spiro compound **1** were obtained from the ^{13}C NMR variable temperature experiments. Figure 5 displays selected aromatic and aliphatic regions at different temperatures ranging from 218 to 328 K. From analysis of the aliphatic region it is apparent that the CH_3 signal is at $\delta = 19.9$ ppm, the CH_2 signal at $\delta = 36.1$ ppm, and the quaternary carbon signal at $\delta = 25.7$ ppm. It is interesting that at higher temperature (328 K) at this same relaxation delay the quaternary carbon resonance disappeared likely because of much longer T_1 compared to other signals. As in the case of proton spectra, when the sample is cooled the ring dynamics is slowed down. At 218 K two signals of the CH_2 carbons at $\delta = 37.0$ ppm and $\delta = 35.2$ ppm are seen evidencing different geometry of both rings. An inspection of the spectra clearly reveals that at 75.46 MHz the coalescence temperature is around 280 K. This result is very consistent with the ^{1}H NMR measurements discussed above.

Interesting information can also be obtained from inspection of the aromatic region. At room temperature, because of motional averaging, only one CH aromatic peak at $\delta = 132.0$ ppm and two partially overlapped quaternary signals at $\delta = 137.1$ ppm and $\delta = 136.9$ ppm are monitored. At higher temperature the latter resonances are better separated. At the coalescence temperature (270 K) only very broad and noisy signals can be seen. At low temperature the two CH resonances at $\delta = 133.0$ and $\delta = 131.0$ ppm and four quaternary carbons at $\delta = 138.0$, $\delta = 137.0$, $\delta = 136.8$, and $\delta = 135.2$ ppm are visible. Thus, the ^{13}C NMR results provide unambiguous evidence which confirms that for the system under investigation at low temperature the ring inversion does not contribute to NMR line broadening and conformations are frozen.

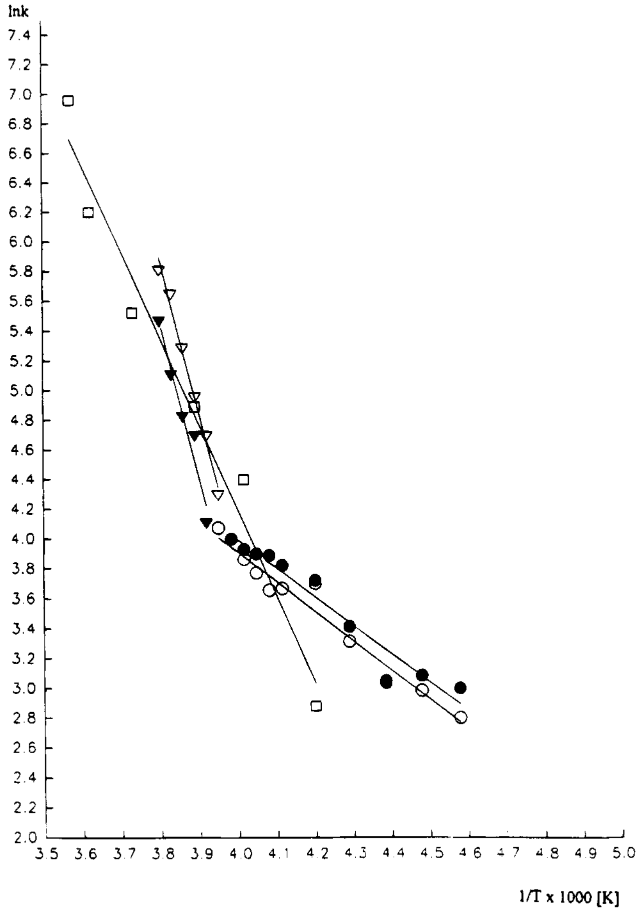

Figure 6. Dependence of the rate constants (ln *k*) of the pseudorotation and inversion of the seven-membered rings of the spiro-compound **1** on $10^3/T$. The experimental points labeled by □ denote ^{13}C-NMR measurements and reflect inversion process. The experimental points given by ○ and ● denote to ^{1}H-NMR measurements and reflect the pseudorotation process below the coalescence temperature. Points labeled by ▽ and ▼ reflect the inversion process above the coalescence temperature (^{1}H-NMR).

Figure 6 displays the relationship between ln *k* and $1/T$. The rate constants ($k = 1/t$) were obtained from line shape analysis of variable temperature ^{1}H and ^{13}C spectra. From both measurements it is apparent that the spiro compound **1** undergoes two processes: pseudorotation at lower temperature and inversion at higher temperature.

Experimental Section

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker 300 MSL spectrometer operating at 300.13 MHz for ^{1}H and 75.468 MHz for ^{13}C, equipped with an Aspect 3000 computer, 160 Mbyte disk, and process controller. The chemical shifts are given in ppm, and the ^{1}H spectra are calibrated with respect to TMS and the ^{13}C with respect to the center of chloroform-*d* set at 77.0 ppm. The accuracy of the spectral line position is estimated to be ±0.05 ppm. Variable temperature experiments were carried out with proton and broadband probeheads and a B-VT1000 variable temperature unit. The temperatures were calibrated employing samples of methanol and ethylene glycol. Total line-shape analysis was carried out to obtain line-time using the expression for classical two-site exchange in a computer program. Iteration was performed by the least-squares procedure; convergent solutions were found on iteration with life-time τ and transverse relaxation time T_2. The initial T_2 values for iteration were obtained from the observed line width for the CH_3 signal. The mass spectra were obtained using a Finnigan Mat 95 spectrometer. The calculations were performed using AM1 and PM3 programs implemented in MOPAC version 6.0 package.

Synthesis of 1,1′,5,5′-Tetrahydro-7,7′,8,8′-tetramethyl-3,3′-spirobi[2,4-benzodithiepin] (1). A solution of sodium trithiocarbonate saturated with hydrogen sulfide was prepared by passing hydrogen sulfide through a solution of sodium ethoxide (2.3 g of Na, 0.1 mol) and carbon disulfide (5.0 g, 0.066 mol) in ethanol (100 mL). This solution was added dropwise to a solution of 1,2-bis(chloromethyl)-4,5-dimethylbenzene (**2**) (10.1 g, 0.05 mol) in ethanol (350 mL). The reaction mixture was allowed to stand overnight. Yellow crystals were filtered off to give the crude product (9.5 g, 94%). Crystallization from chloroform gave an analytically pure sample of **1**: mp 255–258 °C; HRMS (EI) M^+ calcd for $C_{21}H_{24}S_4$ 404.0761, obsd 404.0765. Anal. Calcd for $C_{21}H_{24}S_4$ (404.66): C, 62.33; H, 5.98; S, 31.69. Found: C, 62.19; H, 5.95; S, 31.70.

Determination of the Crystal Structure of 1.[23] The crystal data and experimental details are presented in Table 4. Intensity data were collected using a CAD4 diffractometer with graphite-monochromatized MoKα radiation. Lattice constants were refined by least-squares fit of 25 reflections in the θ range 7.80–11.99°.

The structure was solved by a SHELXS-86 program,[20] and then 2134 observed reflections [$I \geq 3\sigma(I)$] were used to refine it by full-matrix least-squares using F's; H atoms were placed geometrically at idealized positions with fixed isotropic thermal parameters equal to 1.3 of isotropic thermal parameter of parent atom and set as riding, and anisotropic thermal parameters were applied for non-hydrogen atoms. The refinement converged to $R = 0.042$ with the unit weight for 226 refined parameters; the largest shift/error in the last cycle was 0.01; the largest residual peak in final difference Fourier map was 0.33 e Å^{-3}. All calculations, except solution by direct methods, were carried out with the Enraf-Nonius SDP crystallographic computing package.[21] Scattering factors were taken from *International Tables for X-ray Crystallography*.[22]

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(20) Sheldrick, G. M.; Krüger, G. M.; Goddard, R. SHELXS-86. *Crystallographic Computing 3*; Oxford University Press: Oxford, 1985.

(21) Frenz, B. A. *SDP—Structure Determination Package*; Enraf-Nonius: Delft, Holland, 1984.

(22) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974.

(23) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.