Organic and Biological Chemistry

Conformational Analysis in Multisulfur Heterocycles. IV. Duplodithioacetone and 3,3:6,6-Bis(tetramethylene)-s-tetrathiane

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Abstract: Variable-temperature nuclear magnetic resonance (nmr) spectroscopy has provided uniquely unequivocal evidence for a drastically lowered chair/twist energy difference in s-tetrathianes. The chair:twist ratio *in solution* is 1.0:2.6 for tetramethyl-s-tetrathiane ("duplodithioacetone") at $-15°$ and 4:1 for 3,3:6,6-bis(tetramethylene)-s-tetrathiane at $0°$. The barrier $(\Delta G^{\neq})$ to chair/twist equilibration in s-tetrathianes is approximately 16 kcal/mole. A method for the preparation of the conformationally pure twist form of duplodithioacetone is described. A combination of the *syn*-axial and *gem*-dialkyl effects is proposed to account for the variation in the chair:twist ratio in a number of multisulfur heterocycles.

Almost 80 years ago, Sachse postulated that cyclohexane could exist in the *rigid chair* conformation (I) or in a *flexible* form capable of assuming the two extreme true boat (II) and twist (III) conformations.[1]

Theoretical calculations[2] and some experimental data[3] indicate that the twist and true boat forms are ~5 and ~10 kcal/mole, respectively, higher in energy than the chair conformer of cyclohexane. It is apparent that a plenitude of increased nonbonded compressions between carbon–hydrogen bonds in the twist and the boat render them higher in energy than the chair. In the numerous reports concerning the measurement of the barrier $(\Delta G^{\neq})$ to chair/chair equilibration in cyclohexane,[4] the twist is usually assumed to be a discrete intermediate. However, the high energy difference between the chair and the twist or the boat form of cyclohexane renders the detection of such unstable species as the twist essentially impossible by common spectroscopic techniques, *e.g.*, nuclear magnetic resonance (nmr). Certain structural modifications of the cyclohexane ring, *e.g.*, the introduction of sp²-hybridized carbon atoms[5] and/or large substituents oriented in a specific manner,[6]

will lower the chair/twist energy difference in cyclohexane.

It is intriguing to consider what effect the introduction of a heteroatom or many heteroatoms into a 6-ring would have on the chair/twist energy difference. A perusal of available compilations of rotational barriers in simple molecules containing different central atoms[7] indicates significant variations in the magnitude of nonbonded interactions from one compound to another. Indeed, the apparently high potential maximum for the *cis* configuration of hydrazine[8] or hydrogen peroxide[9] attests to the significant lone pair–lone pair repulsions present in these molecules and others.[10] These variations lead naturally to a prediction of differences in the chair/twist energy difference in a number of 6-rings containing different atoms. Although some evidence is available that heteroatoms distort the 6-ring from a true chair conformation,[11] and certain "loaded" systems prefer a twist or boat form,[12] the vast majority of simple 6-rings containing heteroatoms prefer the chair conformer.[12] Even the multiheteroatomic 6-rings, acetone diperoxide (IV)[13] and N,N',N'',N'''-tetramethylhexahydrotetrazine (V),[14] prefer the chair conformation, al-
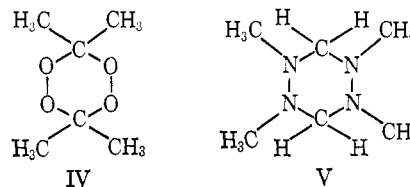
(1) H. Sachse, *Ber.*, **23**, 1363 (1890); *Z. Phys. Chem.* (Leipzig), **10**, 203 (1892).

(2) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961); C. W. Beckett, K. S. Pitzer, and R. Spitzer, *ibid.*, **69**, 2488 (1947); C. W. Beckett, N. K. Freeman, and K. S. Pitzer, *ibid.*, **70**, 4227 (1948); R. B. Turner, *ibid.*, **74**, 211 (1952); K. E. Howlett, *J. Chem. Soc.*, 4353 (1957).

(3) W. S. Johnson, J. L. Margrave, V. J. Bauer, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Am. Chem. Soc.*, **82**, 1255 (1960); N. L. Allinger and L. A. Freiberg, *ibid.*, **82**, 2393 (1960).

(4) F. A. L. Anet and A. J. R. Bourn, *ibid.*, **89**, 760 (1967); F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *ibid.*, **84**, 386 (1962).

(5) N. L. Allinger, J. Allinger, and M. A. DaRooge, *ibid.*, **86**, 4061 (1964); W. D. Kumler and A. C. Huitric, *ibid.*, **78**, 3369, 1147, 614 (1956); F. Lautenschaeger and A. F. Wright, *Can. J. Chem.*, **41**, 1972 (1963).

(6) N. L. Allinger, and H. M. Blatter, *J. Am. Chem. Soc.*, **83**, 994 (1961); H. Booth and G. C. Gidley, *Tetrahedron Letters*, 1449 (1964).

(7) E. B. Wilson, *Proc. Nat. Acad. Sci. U. S.*, **43**, 816 (1957); S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York, N. Y., 1954.

(8) A. Veillard, *Theor. Chim. Acta*, **5**, 413 (1966).

(9) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(10) R. L. Collin and W. N. Lipscomb, *Acta Cryst.*, **4**, 10 (1951); E. A. Myers and W. N. Lipscomb, *ibid.*, **8**, 583 (1955).

(11) J. B. Lambert and R. A. Keske, *Tetrahedron Letters*, 4755 (1967); J. B. Lambert, R. G. Keske, and D. K. Weary, *J. Am. Chem. Soc.*, **89**, 5921 (1967); J. B. Lambert, *ibid.*, **89**, 1836 (1967).

(12) F. A. Riddell, *Quart. Rev.* (London), **21**, 364 (1967).

(13) R. W. Murray, P. R. Story, and M. L. Kaplan, *J. Am. Chem. Soc.*, **88**, 526 (1966).

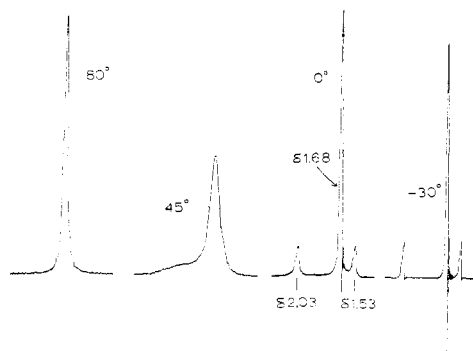(14) J. E. Anderson and J. D. Roberts, *ibid.*, **90**, 4186 (1968).

Figure 1. The nmr spectrum (60 MHz) of duplodithioacetone (VI) at various temperatures.

The large singlet resonance (δ 1.68 ppm, Figure 1) is assigned to the twist conformer (D_2 symmetry) in which

though V displays somewhat unique behavior with two methyl groups in axial positions.

This paper concerns a study of the effect of extensive introduction of divalent sulfur into the 6-ring. Indeed, we report here the uniquely unequivocal measurement of an unusually low chair/twist energy difference in tetramethyl-s-tetrathiane ("duplodithioacetone," VI)[15a] and in 3,3:6,6-bis(tetramethylene)-s-tetrathiane (VII)[15b] as well as the isolation *in solution* of the conformationally pure twist form of duplodithioacetone.[15c] The ef-

VI   VII
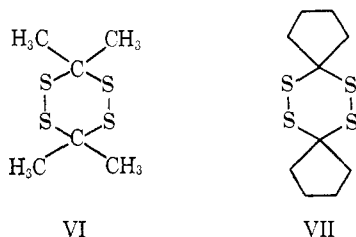
fects of elongated sulfur–sulfur (2.08 Å) and carbon–sulfur (1.80 Å) bonds[16] and lone pair–lone pair interactions are evident.

Results and Interpretation

Examination of the nmr spectrum (60 MHz) of duplodithioacetone[17] (VI, 15% by weight in tetrachloroethylene or carbon disulfide) at 35° reveals two broad resonances (δ 2.00 and 1.66 ppm) of unequal intensity. Upon lowering the temperature, the resonances sharpened in a manner characteristic of a decreasing rate of exchange on the nmr time scale into *two small singlets* (δ *1.53 and 2.03 ppm*) *of equal area* and a larger singlet at δ 1.68 ppm (Figure 1). Upon raising the sample temperature, the spectrum exhibited broadening characteristic of an increasing rate of exchange on the nmr time scale until the total spectrum had coalesced to a single resonance (δ 1.73 ppm) at about 80° (Figure 1). Upon lowering the temperature, an identical sequence of spectral transitions was observed.
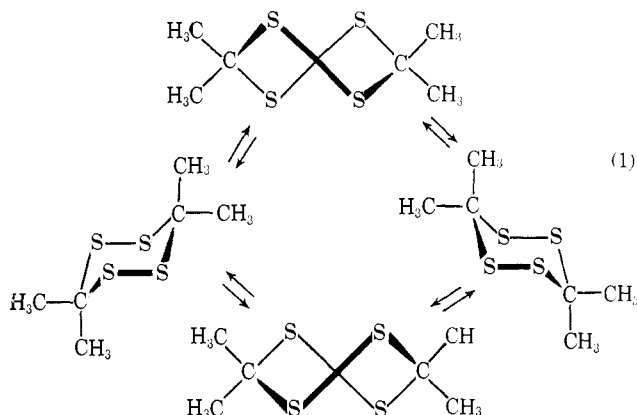
The above observations would seem to be best rationalized by the presence of a *stable twist form of duplodithioacetone* in equilibrium with the *less stable chair conformer* (eq 1). Indeed, there are two equivalent forms each of the chair and twist conformers (eq 1).

all methyl groups are equivalent. By analogy with chemical shift trends in other 6-rings[18] and assuming that the diamagnetic anisotropy of the sulfur–sulfur bond is analogous (possibly enhanced?) to that proposed for the carbon–carbon bond in cyclohexane,[19] the peak at δ 1.53 ppm (Figure 1) is assigned to the axial methyl of the chair conformer (C_{2h} symmetry) and the other resonance of equal area (δ 2.03 ppm) to the equatorial methyl. Consideration of eq 1 will indicate that a given methyl group can exchange among all three chemical environments in the system. Consequently, under conditions of rapid exchange on the nmr time scale, e.g., at 80° (Figure 1), the total nmr spectrum of duplodithioacetone should time average to a single line.

At −15° in carbon disulfide, the chair/twist ratio for duplodithioacetone (0.8 M) is 1.0:2.6. From the temperature dependence of the nmr spectrum of duplodithioacetone (Figure 1), the free energy of activation ($\Delta G^{\ddagger}$) for the chair to boat process is estimated to be 16 ± 1 kcal/mole at 50°.[20]

The nmr spectrum of the spiro structure, 3,3:6,6-bis(tetramethylene)-s-tetrathiane (VII),[17] was also observed to be markedly temperature dependent. Examination of the nmr spectrum of VII (10% by weight in tetrachloroethylene) at 37° reveals two broadened resonances of substantially different intensity centered at δ 2.60 ppm and 1.70 ppm (Figure 2). When the temperature was lowered to 0°, the two resonances sharpened to give a rough triplet (δ 2.64 ppm) and a larger multiplet (δ 1.70 ppm). The ratio of the areas of the low-field resonance (δ 2.64 ppm) to the high-field resonance (δ 1.70 ppm) is 1:4 at 0° (Figure 2). When the temperature was raised above 37°, further broadening of the two resonances was observed. The low-field peak (δ 2.64 ppm) began to coalesce with another resonance originally centered at low temperature under the large multiplet (δ 1.70 ppm). At 100°, these two signals had coalesced to a broad resonance (δ 2.17 ppm). The area ratio of the low-field resonance to the high-field resonance is approximately 1:1 (some overlap) at 100°

(15) (a) C. H. Bushweller, *J. Am. Chem. Soc.*, **89**, 5978 (1967); (b) C. H. Bushweller, *ibid.*, **90**, 2450 (1968); (c) C. H. Bushweller, *Tetrahedron Letters*, 2785 (1968).

(16) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962.

(17) B. Magnusson, *Acta Chem. Scand.*, **13**, 1031 (1959).

(18) R. H. Bible, Jr., "Interpretation of NMR Spectra, An Empirical Approach," Plenum Press, New York, N. Y., 1965.

(19) A. A. Bothner-By and C. Naar-Colin, *Ann. N. Y. Acad. Sci.*, **70**, 833 (1958).

(20) A detailed study of the rate processes involved in the chair/twist equilibration by comparison of experimental spectra with computer-generated standard spectra and by direct measurement of the rate of equilibration of the available pure twist conformer will appear in a subsequent report.
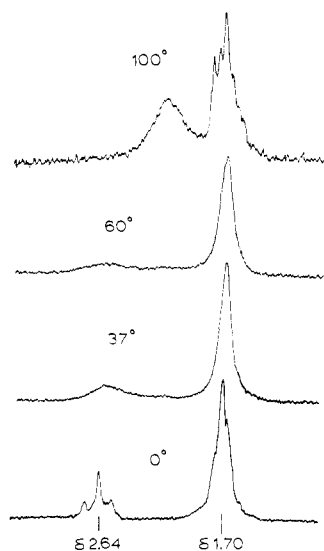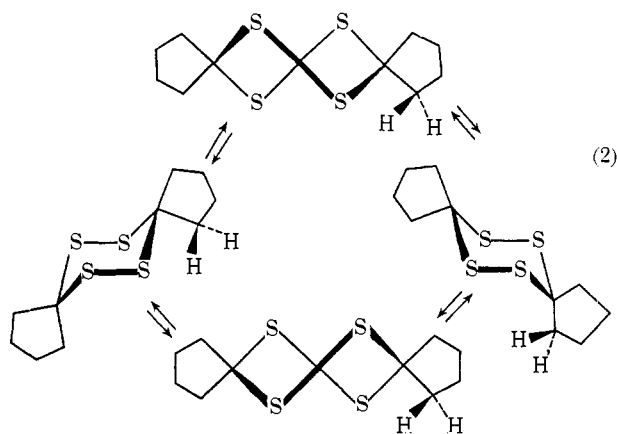
Figure 2. The nmr spectrum (60 MHz) of 3,3:6,6-bis(tetra-methylene)-s-tetrathiane (VII) at various temperatures.

(Figure 2). Upon lowering the temperature, an identical sequence of spectral events was observed.

Such spectral behavior would seem to be best accommodated by a chair/twist equilibrium in VII with a *predominance of the chair conformer* (eq 2). The two reso-

(2)

nances which coalesce with increasing temperature are assigned to the equatorial and axial α-methylene protons of the chair conformer (eq 2).[20] As in the case of duplodithioacetone, if the diamagnetic anisotropy of the sulfur–sulfur bond is analogous to that proposed for the carbon–carbon bond in cyclohexane,[19] the resonance at δ 2.64 ppm observed at $0°$ may be assigned to the equatorial α-methylene group.[21] If VII existed exclusively as the chair conformer, the peak area ratio at $0°$ would be expected to be 1:3. The observed deviation (1:4) suggests the presence of the twist conformer (eq 2). The α-methylene proton resonances of the twist form as well as the axial α-methylene protons peak of the chair would be expected by analogy to be a part of the large multiplet (δ 1.70 ppm). This analysis produces a

(21) An alternative rationalization for the temperature dependence of the nmr spectrum of VII is a predominance of the twist form having a *high barrier to pseudorotation.* The nonequivalence of the two protons in each α-methylene group is evident from a consideration of a model of the twist form. Although current data do not unequivocally rule out such a possibility, we consider it unlikely. Examination of appropriately deuterated species will provide an unequivocal answer.[15c]
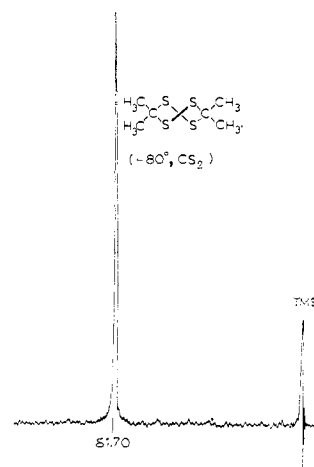
chair:twist ratio of 4:1 for VII (tetrachloroethylene at $0°$).

The substantial barrier to chair/twist equilibration in duplodithioacetone ($\Delta G^{\neq} \cong 16$ kcal/mole) suggests that at an appropriately low temperature, the half-lives ($t_{1/2}$) of the chair and twist conformers are quite long (many hours), *i.e.*, they are effectively separate compounds isolable by some technique. By making the admittedly crude approximation that the entropy of activation ($\Delta S^{\neq}$) for the chair/twist process is zero ($\Delta H^{\neq} \cong 16$ kcal/mole), the half-life of the twist form can be estimated at various temperatures (Table I). It is ap-

Figure 3. The nmr spectrum (60 MHz) of the conformationally pure twist form of duplodithioacetone.

Table I. Estimated Half-Life of the Twist Form of Duplodithioacetone at Various Temperatures ($\Delta H^{\neq} \sim 16$ kcal/mole; $\Delta S^{\neq} \sim 0$ eu)

| | Temperature, °C | | |
	25	−30	−80
$t_{1/2}$	0.07 sec	35 sec	75 hr

parent that at about $-80°$, the half-life of the twist is long enough to permit isolation. Indeed, the isolation was achieved by capitalizing on the conformational purity of crystalline duplodithioacetone. By cooling a sample of *crystalline* duplodithioacetone to $-80°$, and then slowly adding carbon disulfide until the sample was *completely dissolved* at $-80°$, the conformationally pure ($\sim 100\%$) twist form of duplodithioacetone was isolated *in solution*. The nmr spectrum of the resultant solution at $-80°$ revealed one sharp singlet resonance (δ 1.70 ppm) and no indication of the two resonances (δ 1.53, 2.03 ppm) of the chair form (Figure 3). Upon warming the sample to $-30°$, the two resonances at δ 2.03 and 1.53 ppm appeared and grew rapidly in intensity.

The uniquely simple and unequivocal nmr spectrum of duplodithioacetone (Figure 1) provides an unusual opportunity to measure accurately the equilibrium constant for a chair/twist system. Thus we have measured the chair/twist ratio in a number of solvents. The various equilibrium constants and associated free energies ($\Delta G°$) are compiled in Table II.[22]

(22) In a prior communication,[15a] the chair–twist free energy difference was calculated incorrectly, assuming two equivalent chair con-
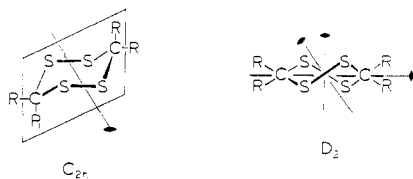
Figure 4. The symmetry properties of the chair and twist forms of s-tetrathianes.

Discussion

The data above provide uniquely unequivocal evidence for a low chair/twist energy difference in a relatively simple, unencumbered 6-ring. If no bond breaking occurs in the course of chair/twist equilibration in s-tetrathianes, one is compelled to postulate the twist as the intermediate in the chair/chair inversion process (eq 1). *Indeed, in the case of duplodithioacetone, the twist is more stable than the chair* (Table II). This ob-

Table II. Thermodynamic Parameters for the Chair/Twist Equilibrium in Duplodithioacetone in Various Solvents

Solvent	K ([twist]/[chair])[a]	$\Delta G°$, kcal/mole
Carbon disulfide	2.6 ± 0.2	0.49 ± 0.05
cis-1,2-Dichloroethylene	3.0 ± 0.2	0.57 ± 0.05
trans-1,2-Dichloroethylene	3.0 ± 0.2	0.57 ± 0.05
1,2-Dimethoxyethane	3.1 ± 0.2	0.58 ± 0.05
Pyridine	3.2 ± 0.2	0.60 ± 0.05
Methylene chloride	3.2 ± 0.2	0.60 ± 0.05
Chloroform	3.3 ± 0.2	0.62 ± 0.05
Tetrachloroethylene	2.7 ± 0.2[b]	0.54 ± 0.05
Acetone-d_6	3.0 ± 0.2[b]	0.60 ± 0.05

[a] $T = 258 ± 4°K$; [duplodithioacetone] = 0.8 M. [b] $T = 273 ± 4°K$; [duplodithioacetone] = 0.4 M.

servation is especially intriguing in light of the plenitude of "saturated" 6-rings, heterocyclic and carbocyclic, which prefer the chair form.[12,23]

The long sulfur–sulfur (2.08 Å)[16] and carbon–sulfur (1.80 Å)[16] bonds in s-tetrathianes must play a role in decreasing vicinal lone-pair repulsions in the twist form. s-Tetrathianes are devoid of classic Pitzer strain, *i.e.*, carbon–hydrogen bond eclipsings, important in increasing the energy of the twist in carbocycles. Entropy effects[24] should favor the twist over the chair form of s-tetrathianes. The chair conformer possesses a twofold proper rotation axis and a horizontal mirror plane giving C_{2h} symmetry (Figure 4) and has a *rigid* structure. The twist has three mutually perpendicular twofold proper rotation axes (D_2 symmetry) making it more symmetrical than the chair (Figure 4). The twist is a *flexible* structure capable of facile torsional motions if not facile pseudorotation.

The above effects are reasonable to account for a lowered chair/twist energy difference in s-tetrathianes, after the fact. However, a perusal of Table III indicates significant *variations* in the chair/twist ratio in a

formers and *one* twist. Indeed, there are *two* equivalent twist forms. Thus the equilibrium constants (Table II) reported here are the same as the twist–chair ratio taken directly from the nmr spectrum. However, entropy may favor the *flexible* twist form over the *rigid* chair.

(23) D. L. Robinson and D. W. Theobald, *Quart. Rev.* (London), 21, 314 (1967).

(24) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience Publishers, New York, N. Y., 1965.

Table III. The Chair : Twist Ratios in Solution for a Number of Multisulfur Heterocycles

Compound	% chair
	27
	80
	100
	100

[a] F. Fehér, B. Degen, and B. Söhngen, *Angew. Chem.*, 80, 320 (1968). [b] H. Köpf, B. Block, and M. Schmidt, *Chem. Ber.*, 101, 272 (1968).

number of multisulfur heterocycles. We believe that two other phenomena are instrumental in tipping the energy balance toward the twist form in s-tetrathianes, *i.e.*, the *gem*-dialkyl effect (Thorpe–Ingold hypothesis of valency deviation)[25] and the *syn*-axial effect ("rabbit-ear" effect).[26]

The consequences of the *gem*-dialkyl effect in s-tetrathianes can be illustrated by consideration of structure VIII. As the steric bulk of the "R" group increases, the RCR bond angle (α) will increase, while the SCS bond angle (θ) will decrease, *i.e.*, S-1 and S-5 move
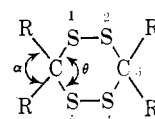
VIII

closer together. This behavior would apply to both the chair and twist conformers.

The *syn*-axial effect[26] arises from nonbonded repulsions between "parallel" lone pairs of electrons located on nonadjacent atoms. Apparently, the repulsions are caused by interaction between lone pair moments[27] on the relevant atoms. The effect is widespread[26] and must be considered important in the "anomalous" occurrence of axial N-methyl groups in N,N′,N″,N‴-tetramethylhexahydrotetrazine (V)[14] and in N,N′-dimethyl-1,3-diazanes.[26]

We believe that the *syn*-axial effect is important in s-tetrathianes. Assuming that divalent sulfur is approximately tetrahedrally hybridized with some distortion due to lone pair repulsions on the same sulfur atom[28] and that the lone pair engenders an electric dipole, consider an "end-on" view of the chair form of an s-tetrathiane (X, XI). In X, the orientation of the lone

(25) (a) P. von R. Schleyer, *J. Am. Chem. Soc.*, 83, 1368 (1961); (b) T. C. Bruice and W. C. Bradbury, *ibid.*, 90, 3808 (1968).

(26) R. O. Hutchins, L. D. Kopp, and E. L. Eliel, *ibid.*, 90, 7174 (1968).

(27) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1966, pp 110–111.

(28) R. J. Gillespie, *Angew. Chem. Intern. Ed. Engl.*, 6, 819 (1967).

pairs is represented, and in XI, the direction of the lone pair moments. In XI, the repulsive interaction between

X   XI
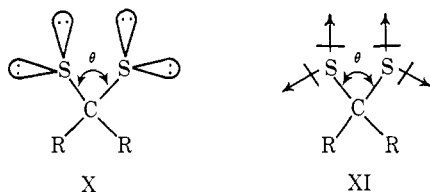
1,3 *syn*-axial lone pair moments (*syn*-axial effect) in the chair form will increase as θ decreases, *i.e.*, as the size of the R group increases (*gem*-dialkyl effect). The increased repulsion can be alleviated by conversion to the twist conformer in which *syn*-axial lone pair moments are less parallel (eq 3). *Of course, as the SCS bond angle*

chair   twist   (3)
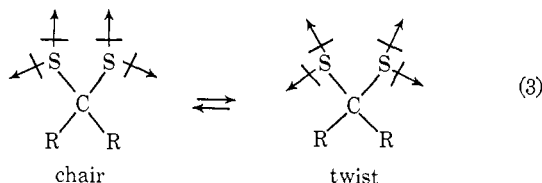
(*θ, XI*) *increases, syn-axial repulsions decrease and twisting becomes less necessary.* Perusal of Table III indicates that as 1,3-sulfur atoms move apart as a consequence of the *gem*-dialkyl effect or longer bonds (*e.g.*, Ti–S), the percentage of the chair conformer increases. The large methyl groups in duplodithioacetone will exert a significant *gem*-dialkyl effect favoring formation of the twist, whereas the effect would be attenuated in 3,3:6,6-bis(tetramethylene)-*s*-tetrathiane (VII) by pinning back the geminal carbon atoms *via* incorporation in the 5-ring. The *syn*-axial effect may also be important in the observation of a small amount ($\sim 10\%$) of the twist form of benzo-4,5,6-trithiacycloheptene.[29]

In converting to the twist, *vicinal lone pairs* in *s*-tetrathianes become *more eclipsed*. The increased eclipsing would presumably raise the energy of the twist conformer. Available data concerning ketone diperoxides, *e.g.*, acetone diperoxide (IV), indicate exclusive preference for the chair conformer.[12,13] It would seem that vicinal lone pair repulsions are more serious than *syn*-axial lone pair repulsions in ketone diperoxides. Indeed, the different dihedral angles in H_2O_2 ($\sim 90°$)[9] and H_2S_2 ($\sim 103°$)[16] suggest enhanced vicinal lone pair repulsions in H_2O_2 as compared to H_2S_2. The short oxygen–oxygen bond length (~ 1.48 Å)[9] and long sulfur–sulfur bond length (2.08 Å)[16] appear to be instrumental in the different vicinal lone pair repulsions.

The *syn*-axial effect is instrumental, at least in part, in causing the unusual preference of N-methyl groups for the axial position in N,N'-dimethyl-1,3-diazanes[26] and N,N',N'',N'''-tetramethylhexahydrotetrazine (IV)[14] with the 6-rings in these cases adopting the chair conformer. However, in these cases, *syn*-axial interactions as well as vicinal nonbonded compressions can be relieved by *inversion about nitrogen*. This option is not available to *s*-tetrathianes which can relieve *syn*-axial interactions in the chair form only by conversion to the twist.

Although a detailed discussion of the conformational dynamics of chair/twist equilibration in *s*-tetrathianes

will be left to a subsequent report,[20] the substantial barrier ($\Delta G^{\neq} \cong 16$ kcal/mole) to chair/twist interconversion deserves some consideration here. The high barrier in *s*-tetrathianes is not atypical of other 6-rings containing adjacent atoms possessing lone pairs of electrons, *e.g.*, acetone diperoxide ($\Delta G^{\neq} = 15.4$ kcal/mole at $30°$),[13] 3,3,6,6-tetramethyl-1,2-dithiane ($\Delta G^{\neq} = 13.8$ kcal/mole at $-2°$),[30] 3,3,6,6-tetramethyl-1,2-dioxane ($\Delta G^{\neq} = 14.6$ kcal/mole at $12°$),[30] N,N',N'',N'''-tetramethylhexahydrotetrazine ($\Delta G^{\neq} = 11.7$ kcal/mole).[14] It would appear that lone pair–lone pair repulsions are instrumental in increasing the barriers in such heterocycles as compared to cyclohexane ($\Delta G^{\neq} = 10.3$ kcal/mole at $-67°$)[4] or 1,1,4,4-tetramethylcyclohexane ($\Delta G^{\neq} = 11.4-11.6$ kcal/mole at $-65°$).[31] Indeed, the importance of lone pair–lone pair repulsions cannot be ignored in a rationalization of the apparently high potential maximum for the *cis* configuration of hydrogen peroxide (~ 7.0 kcal/mole),[32] hydrazine (~ 11.5 kcal/mole),[8] and hydrogen disulfide (5.6 kcal/mole).[9] It is also apparent that lone pair repulsions are a factor in the preferred conformation of hydroxylamine (nitrogen lone pair and oxygen–hydrogen bond eclipsed).[10]

Although many studies have dealt with the measurement of the rate of very fast conformational equilibrations in solution, little effort has been expended to isolate conformers in solution when the barrier ($\Delta G^{\neq}$) to conformational equilibration is ~ 16 kcal/mole or less, *i.e.*, equilibration is rapid at room temperature.[33] The isolation of the conformationally pure twist form of duplodithioacetone at $\sim -80°$ represents one of these unique cases. The isolation of a single conformer, *i.e.*, the twist, at low temperature strongly implies the conformational homogeneity of crystalline duplodithioacetone and is consistent with X-ray crystallographic data of Fredga[34] indicating that crystalline duplodithioacetone is conformationally pure as a true boat conformer (XVI) with a sulfur atom at each prow position. Formation of the twist in solution from the crystalline true boat form can be achieved *via* a low barrier twisting process. The singlet resonance (δ 1.70, Figure 3) observed for the conformationally pure twist form of

XVI
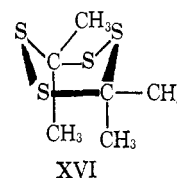
duplodithioacetone at $-80°$ is consistent with a symmetrical, nonpseudo-rotating twist (D_2 symmetry; all methyls equivalent) *or* a rapidly pseudorotating twist. If pseudorotation is slow on the nmr time scale, the presence of a true boat (XVI) in solution is not consistent with a singlet nmr signal as a chemical shift between geminal methyls would be expected.

(30) G. Claeson, G. Androes, and M. Calvin, *J. Am. Chem. Soc.*, **83**, 4357 (1961).

(31) (a) R. W. Murray and M. L. Kaplan, *Tetrahedron*, **23**, 1575 (1967); (b) W. Reusch and D. F. Anderson, *ibid.*, **22**, 583 (1966); (c) H. Friebolin, W. Faisst, and H. S. Schmid, *Tetrahedron Letters*, 1317 (1966).

(32) R. H. Hunt, R. A. Leacock, C. W. Peters, and K. T. Hecht, *J. Chem. Phys.*, **42**, 1931 (1965).

(33) F. R. Jensen and C. H. Bushweller, *J. Am. Chem. Soc.*, **88**, 4279 (1966).

(34) A. Fredga, *Acta Chem. Scand.*, **12**, 891 (1958).

(29) S. Kabuss, A. Luttringhaus, H. Friebolin, and R. Mecke, *Z. Naturforsch.*, **216**, 320 (1966).

There is a paucity of data concerning the conformational idiosyncrasies of spiro structures. Theoretical calculations indicate that bond angle distortions of the type present in spiro compounds are important in conformational equilibria.[35] The limited number of reports concerning spiro structures indicate marked deviations from trends in open-chain analogs.[36] The significant reduction in the amount of twist conformer in 3,3:6,6-bis(tetramethylene)-s-tetrathiane (VII) as compared to duplodithioacetone (VI) is evidence of the uniqueness of the spiro analog. The preference for the chair form in VII is consistent with a preliminary X-ray crystallographic study indicating the presence of the chair form.[37]

The results of a study of the solvent dependence of the twist/chair ratio in duplodithioacetone (Table II) are not

unexpected, i.e., no appreciable solvent effect. It is noteworthy that in a nonpolar solvent (trans-1,2-dichloroethylene) and a highly polar solvent (cis-1,2-dichloroethylene), the chair:twist ratio is the same.

Experimental Section

Nmr spectra were recorded using a Varian A-60 spectrometer equipped with a V-6040 temperature controller. Temperature was measured using a methanol or ethylene glycol sample.

Duplodithioacetone was prepared according to the method of Magnusson.[17] *Anal.* Calcd for $C_6H_{12}S_4$: C, 33.95; H, 5.70; S, 60.02. Found: C, 33.98; H, 5.83; S, 60.02.

3,3:6,6-Bis(tetramethylene)-s-tetrathiane was prepared according to the method of Magnusson.[17] *Anal.* Calcd for $C_{10}H_{16}S_4$: C, 45.41; H, 6.10; S, 48.49. Found: C, 45.44; H, 6.14; S, 48.59.

Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory.

(35) J. B. Hendrickson, *J. Am. Chem. Soc.*, 84, 3355 (1962).
(36) (a) R. A. Carlson and N. S. Behn, *Chem. Commun.*, 339 (1968); (b) J. J. Uebel, *Tetrahedron Letters*, 4751 (1967).
(37) D. S. Breslow and H. Skolnik, "Multi-Sulfur and Sulfur and Oxygen Five- and Six-Membered Heterocycles," Part Two, Interscience Publishers, New York, N. Y., 1966, p 629.

Cage Effects and Activation Volumes for Homolytic Scission Reactions[1,2]

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Abstract: The effects of pressure on the rates of solution phase decomposition of the *t*-butyl peresters of phenylacetic acid, cyclohexanecarboxylic acid, and benzoic acid have been determined, as well as the pressure dependence of the product distributions of the first two peresters. In cumene at 79.6°, the observed activation volumes are *t*-butyl perbenzoate, +10 cc/mole; carbo-*t*-butylperoxycyclohexane, +3.9 cc/mole; and *t*-butyl phenylperacetate, +1 to +3 cc/mole. The data are used to demonstrate that observed activation volumes are abnormally high for homolytic scission reactions in which cage recombination of the primary radical products can occur to regenerate starting material. Product data support the mechanistic proposals and additionally permit calculations of crude values for the difference in activation volumes for radical combination, disproportionation, and diffusion.

Solution phase decomposition of radical initiators such as azo compounds, diacyl peroxides, and peresters often gives less than a stoichiometric yield of kinetically free radicals which can initiate polymerization, autoxidation, or other radical reactions. This apparent inefficiency in radical production indicates that the radical pair arising from a molecule of initiator remains in a solvent shell long enough to undergo bimolecular coupling or disproportionation reactions in competition with separative diffusion.[3]
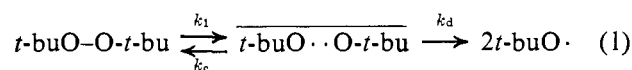
This manifestation of the cage effect has long been recognized and studied because of its kinetic visibility.

Another potential manifestation of the cage effect, not readily observable, is illustrated in eq 1 using *t*-butyl peroxide (DBO) as the example. While the ultimate yield of kinetically free *t*-butoxy radicals from DBO is

$$t\text{-buO-O-}t\text{-bu} \underset{k_c}{\overset{k_1}{\rightleftharpoons}} \overline{t\text{-buO}\cdots\text{O-}t\text{-bu}} \overset{k_d}{\longrightarrow} 2t\text{-buO}\cdot \quad (1)$$

quantitative, the apparent rate constant for DBO decomposition is not necessarily equal to that for homolytic scission (k_1). Rather it is given by the expression in eq 2 and will approach k_1 only when $k_c <<< k_d$.

$$k_{\text{obsd}} = k_1\left[\frac{k_d}{k_c + k_d}\right] \quad (2)$$

This specific operation of the cage effect to bring about a regeneration of the free-radical initiator after homolytic scission has been the subject of debate for many years; however, it has only been recently experimentally verified. Martin showed by ^{18}O-labeling studies that such recombination was significant in the