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# Theoretical Studies on Transannular S···S Interactions in Geometrically Constrained 1,5-Dithiocane Derivatives

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**Abstract:** This paper probes, using theoretical calculations, the nature of nonbonded interaction between sulfur functional groups in geometrically constrained 1,5-dithiocane derivatives. Vibronic analysis using SCF/STO-3G* ab initio calculations of the boat conformers of naphtho[1,8-*b*,*c*]-1,5-dithiocin (**1**) and its 1-oxide (**2**), 1,5-dioxide (**3**), 1,1-dioxide (**4**), and 1,1,5-trioxide (**5**) were carried out. The calculated geometries are close to the experimental geometries determined by single-crystal X-ray crystallographic methods. Comparison of the frequencies of the S···S rocking mode for these compounds was used to test whether there is bond formation in **2**–**5**. The results, using this new criterion, show that there is no significant bond formation in **2** and **3** despite the observed geometry changes ascribed to "incipient" bond formation. There is also no attractive interaction in **4** and **5**. The weak attraction in **2** and **3** may be due to dipole or charge-transfer interactions.

## Introduction

Nonbonded interactions are emerging as key factors in determining the geometry of molecules, their reactivity, and their biological properties, but such interactions are only poorly understood. Nonbonded interactions of sulfur are especially interesting in this regard for several reasons. There are numerous examples of conformational control due to such interactions in sulfur compounds. Series of compounds are known in which the S···X distances span the range from no interaction, i.e. the S···X distance is equal to or greater than the sum of their van der Waals radii, through weak interaction, i.e. "incipient" sulfuranes, to strong covalent bonding, i.e. in hypervalent sulfuranes. In addition, sulfur-containing compounds are important biologically. Nonbonded S···O,[1] S···N,[2] S···π,[3] and S···S[4] interactions[5] have all attracted particular interest and, although this paper is concerned specifically with S···S interactions, the methodology developed herein is applicable to studying these other systems. The phenomenon observed experimentally, which this theoretical approach endeavors to interpret, is that the S···X distances are less than the sum of their van der Waals radii and R–S···X angles approach 180°. Previous ab initio theoretical analyses[6,7] have generally used models, rather than real molecules for which the experimental results have been obtained, and focussed on calculation of S···X covalent bond orders which requires translation of quantum chemical results into classical chemical concepts.[6-8] This

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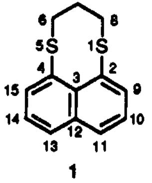
**Table I.** X-ray Data for Compounds **1**–**5**

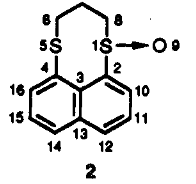
| compd | S(1)···S(5), Å | C(2)–S(1)–O(9), deg | C(8)–S(1)–O(9), deg | S(5)···S(1)–O(9), deg |
|---|---|---|---|---|
| **1** | 3.23 | | | |
| **2** | 3.00 | 104.8 | 102.3 | 174.2 |
| **3** | 3.05 | 106.5 | 103.4 | 170.3 |
| **4** | 3.27 | 106.7 | 104.4 | 172.1 |
| **5** | 3.40 | 106.4 | 103.6 | 177.0 |

translation is fraught with peril with partial covalent bonds such as in S···X systems in which the covalency of S···X interactions is said to range from 0.05 to 0.25 of a bond order.

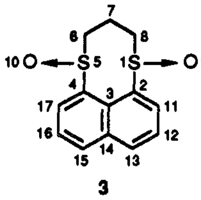
To provide an alternative, stringent test of bond formation in S···X interactions we proposed use of vibronic analysis.[9] Ab initio calculations on real compounds **1** and **2** for which experimental data have been obtained and which suggest "incipient" bond formation in **2** were done at the STO-3G level. The concept is that, if there is covalent bond formation in **2**, but not in **1** then vibrational modes which increase the S···S distance should be higher in frequency in **2** than in **1**. The surprising result was that the frequency for the S···S rocking mode, which increases the S···S distance, was the same in **1** and **2**. However, it has been reported that the inclusion of d orbitals in the basis set is essential for describing the covalency in S···O[6] and S···N[7] interactions and they are of importance in hypervalent bonding of sulfur.[10] In addition, the calculated SO bond length in **2** and SO stretching frequency are in error. Consequently, it was imperative to perform the calculations on **1** and **2** with d orbitals in the basis set. This paper reports these extended calculations which mandated the extensive use of an IBM 3090 Supercomputer because ab initio calculations at the STO-3G* level were done on the actual molecules **1** and **2**. In addition, these studies were extended to **3**–**5** to fully explore S···S interactions for which experimental data had been obtained.[11]



**1**



**2**



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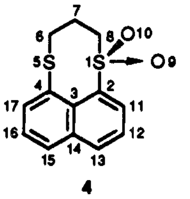
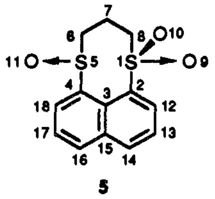


**4**



**5**

## Results

**X-ray Analysis of 1–5.** The X-ray crystallographic structure of **1** has been reported[11] and those of **2**–**5** will be reported elsewhere.[12] X-ray parameters pertinent to this study are listed in Table I. The S···S intramolecular distances of 3.00 and 3.05 Å for compounds **2** and **3**, respectively, are about 0.2 Å closer than the S···S distance in dithioether **1** (3.23 Å). The C(2)–S(1)–O(9) and C(8)–S(1)–O(9) bond angles in compound **2** are 104.2 and 102.3°, and these angles for compound **3** are 106.6 and 104.6°, respectively, which is small compared to the average value of 106.8° for these same relative angles in other six-, seven-, and eight-membered-ring sulfoxides.[9] Furthermore, the S(5)···S(1)–O(9) angle is a near linear 174.2 and 170.3° for compounds **2** and **3**, respectively. Thus the angle distortions about the sulfoxide sulfur atoms in **2** and **3** and the short S···S intramolecular contact for **2** and **3** suggest a distorted trigonal-bipyramidal structure at S(1) with S(5) and O(9) occupying the apical positions.[4] The X-ray structures for compounds **4** and **5** have angular distortions about the S(1)–O(9) bond similar to that described for compounds **2** and **3**; however, the S···S intramolecular distances for **4** (3.27 Å) and **5** (3.40 Å) are larger than the S···S distance in **1** by 0.04 and 0.17 Å, respectively.

**Table II.** Mulliken Atomic Charge Populations Calculated for Sulfur Atoms at the SCF/STO-3G* Level for Compounds **1**–**5**

| compd | S(1) | S(5) |
|---|---|---|
| **1** | 0.05 | 0.05 |
| **2** | 0.05 | 0.30 |
| **3** | 0.06 | 0.39 |
| **4** | 0.30 | 0.30 |
| **5** | 0.33 | 0.38 |

On the basis of this X-ray data compounds **2** and **3** show a stabilizing transannular interaction due to short S···S distances and angle distortions at S(1), whereas compounds **4** and **5** do not show evidence for a stabilizing transannular interaction as revealed by the long S···S distances.

**Theoretical Characterization of the Bond Strength.** There are several ways the strength of the bonding between chemical systems (atoms, molecules) can be qualitatively and quantitatively characterized with the use of quantum chemistry criteria. The most popular and the easiest to calculate is the so called "bond order". The concept of these categories was introduced to chemistry by Mulliken[13] and Chirgwin and Coulson[14] and successfully used for years in theoretical studies on chemical bond formations. The "bond order" is evaluated on the basis of the total one-electron density function, which for the wave function in the form of a single Slater determinant is expressed through products of atomic orbitals and expansion coefficients of the occupied molecular orbitals. As a result of integrating the density function over the entire space one generates the electronic population which one usually attributes to the atoms and the bonds. The total electronic population on an atom then can be calculated by dividing the bond population by 2 and adding it to the atomic populations of both atoms which form the bond. This is the principle of the Mulliken atomic population analysis. The higher bond population is usually attributed to a stronger chemical bond. However, such an approach is known to be very basis set dependent, as is seen from standard equations, and can lead to erroneous conclusions in characterization of the molecular bond structure and the molecular charge distribution. When one examines the Mulliken atomic charge populations on sulfur atoms calculated at the SCF/STO-3G* level (see Table II) for compounds **1**–**5**, one notices a considerable electron flow toward the oxygen atoms, which generates sizable positive net charges on the sulfur atoms. Therefore, one might expect a significant alternation in the type and the strength of the interaction between sulfur atoms when one adds more oxygens. However, the arguments presented later in this paper do not support this conclusion.

The ultimate measure of the strength of the chemical bonding is the energy required to break the bond. This can be readily calculated at various levels of theoretical sophistication. Usually one calculates the energy of the molecule and the energies of the fragments which result from the bond breaking. Difference in the energies gives the bond energy. A problem however arises when one studies the strength of a bond which is formed within the molecule whose breaking does not lead to a separation of the molecule into two independent fragments. The transannular S···S interactions in the 1,5-dithiocane derivatives, which are the subjects

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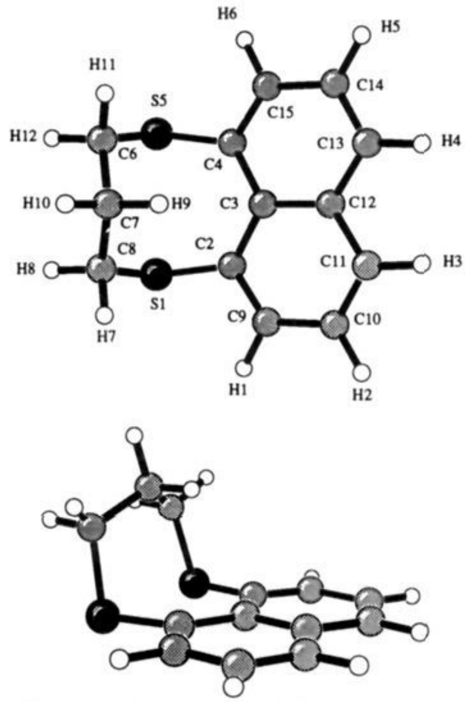

**Figure 1.** Three-dimensional view and labeling scheme for compound **1**.

of the present studies, are perfect examples of such a problem. It is not clear how one should change the relative distance between the sulfur atoms to test the existing interaction without altering the structure of the whole molecule, which may lead to an energy increase not directly related to the interaction of interest. In order to overcome this difficulty we proposed a method which is based on the analysis of the force field of the molecule, by means of the harmonic vibrational frequencies and the normal vibrational modes.[9] These frequencies can be calculated in an ab initio procedure, which utilizes second-order derivatives of the total SCF molecular energy with respect to the nuclear displacements.

$$f_{AB} = \frac{\partial^2 E_{SCF}}{\partial R_A \, \partial R_B} \qquad (1)$$

If there exists an attractive interaction between two atoms in the molecule, this will usually manifest itself by an increase of the vibrational frequency of the mode which corresponds to a change in the separation of these two atoms. For the 1,5-dithiocane systems one should, therefore, examine the theoretically determined vibrational modes and determine which one corresponds to an increase of the S···S separation. If the vibrational energy of this mode increases when more oxygen atoms are bound to the sulfur atoms, one may conclude that the transannular interaction becomes stronger.

The analysis of the intramolecular interactions based on the calculation of the SCF vibrational frequencies for larger molecular systems is computationally a very demanding task in terms of the cpu time and the disk requirement. The present SCF/STO-3G* calculations on 1,5-dithiocane derivatives, performed on the IBM 3090 supercomputer, certainly belong to the most involved ever accomplished at this level of theory.

**Vibronic Analysis.** Vibronic analysis of the boat conformers of compounds **1–5** was carried out by using the SCF method with the STO-3G* basis set.[15] The GAUSSIAN-86 program[16] was used to do these calculations. The nature of the analysis precluded high-level calculations on simplified models of compounds **1–5**.

**Table III.** Optimized Geometry for the Boat Conformation of Compound **1**[a]

| | | | |
|---|---|---|---|
| Interatomic Distances, Å | | | |
| S(1)–C(2) | 1.76 | C(9)–C(10) | 1.42 |
| C(2)–C(3) | 1.46 | C(10)–C(11) | 1.35 |
| C(3)–C(4) | 1.46 | C(11)–C(12) | 1.43 |
| C(4)–S(5) | 1.76 | C(12)–C(13) | 1.43 |
| S(5)–C(6) | 1.79 | C(13)–C(14) | 1.34 |
| C(6)–C(7) | 1.55 | C(14)–C(15) | 1.42 |
| C(7)–C(8) | 1.55 | C(15)–C(4) | 1.37 |
| C(8)–S(1) | 1.79 | C(3)–C(12) | 1.41 |
| C(2)–C(9) | 1.37 | S(1)···S(5) | 3.05 |
| Interatomic Angles, deg | | | |
| S(1)–C(2)–C(3) | 125.1 | C(11)–C(12)–C(13) | 118.8 |
| C(2)–C(3)–C(4) | 124.9 | C(12)–C(13)–C(14) | 120.8 |
| C(3)–C(4)–S(5) | 125.1 | C(13)–C(14)–C(15) | 119.2 |
| C(4)–S(5)–C(6) | 100.7 | C(14)–C(15)–C(4) | 122.7 |
| S(5)–C(6)–C(7) | 116.9 | C(15)–C(4)–C(3) | 119.1 |
| C(6)–C(7)–C(8) | 114.9 | S(1)–C(2)–C(9) | 115.7 |
| C(7)–C(8)–S(1) | 116.9 | S(5)–C(4)–C(15) | 115.7 |
| C(8)–S(1)–C(2) | 100.7 | C(2)–C(3)–C(12) | 117.5 |
| C(2)–C(9)–C(10) | 122.7 | C(4)–C(3)–C(12) | 117.5 |
| C(9)–C(10)–C(11) | 119.2 | C(11)–C(12)–C(3) | 120.6 |
| C(10)–C(11)–C(12) | 120.8 | C(13)–C(12)–C(3) | 120.6 |
| Dihedral Angles, deg | | | |
| S(1)–C(2)–C(3)–C(4) | −3.0 | C(3)–C(2)–C(9)–C(10) | −0.5 |
| C(2)–C(3)–C(4)–S(5) | 2.9 | C(2)–C(9)–C(10)–C(11) | 0.1 |
| C(3)–C(4)–S(5)–C(6) | −82.7 | C(9)–C(10)–C(11)–C(12) | 0.3 |
| C(4)–S(5)–C(6)–C(7) | 53.9 | C(10)–C(11)–C(12)–C(13) | 179.2 |
| S(5)–C(6)–C(7)–C(8) | 57.0 | C(11)–C(12)–C(13)–C(14) | −179.2 |
| C(6)–C(7)–C(8)–S(1) | −57.1 | C(12)–C(13)–C(14)–C(15) | −0.3 |
| C(7)–C(8)–S(1)–C(2) | −53.8 | C(13)–C(14)–C(15)–C(4) | −0.1 |
| C(8)–S(1)–C(2)–C(3) | 82.8 | C(14)–C(15)–C(4)–C(3) | 0.6 |
| C(4)–C(3)–C(2)–C(9) | −179.2 | C(15)–C(4)–C(3)–C(2) | 179.1 |

[a] SCF Energy = −1279.7062042 hartrees. Nuclear repulsion energy = 1204.34509570 hartrees. Rotational constant = 0.7062966, 0.5389405, 0.350606 GHz.

**Table IV.** Optimized Geometry for the Boat Conformer of Compound **2**[a]

| | | | |
|---|---|---|---|
| Interatomic Distances, Å | | | |
| S(1)–C(2) | 1.82 | C(2)–C(3) | 1.45 |
| C(3)–C(4) | 1.45 | C(4)–S(5) | 1.76 |
| S(5)–C(6) | 1.79 | C(6)–C(7) | 1.55 |
| C(7)–C(8) | 1.54 | C(8)–S(1) | 1.84 |
| S(1)–O(9) | 1.48 | C(2)–C(10) | 1.36 |
| C(10)–C(11) | 1.42 | C(11)–C(12) | 1.35 |
| C(12)–C(13) | 1.43 | C(13)–C(14) | 1.43 |
| C(14)–C(15) | 1.35 | C(15)–C(16) | 1.42 |
| C(16)–C(4) | 1.36 | C(3)–C(13) | 1.41 |
| S(1)···S(5) | 2.98 | | |
| Interatomic Angles, deg | | | |
| S(1)–C(2)–C(3) | 125.7 | C(2)–C(3)–C(4) | 124.6 |
| C(3)–C(4)–S(5) | 122.9 | C(4)–S(5)–C(6) | 99.9 |
| S(5)–C(6)–C(7) | 115.1 | C(7)–C(8)–S(1) | 118.4 |
| C(8)–S(1)–C(2) | 97.1 | O(9)–S(1)–C(2) | 106.3 |
| O(9)–S(1)–C(8) | 104.9 | C(2)–C(10)–C(11) | 121.8 |
| C(10)–C(11)–C(12) | 119.4 | C(11)–C(12)–C(13) | 120.8 |
| C(12)–C(13)–C(14) | 119.6 | C(13)–C(14)–C(15) | 120.9 |
| C(14)–C(15)–C(16) | 119.5 | C(16)–C(4)–C(3) | 119.3 |
| S(1)–C(2)–C(10) | 113.9 | S(5)–C(4)–C(16) | 117.7 |
| C(2)–C(3)–C(13) | 117.3 | C(4)–C(3)–C(13) | 118.1 |
| C(12)–C(13)–C(3) | 120.3 | C(14)–C(13)–C(3) | 120.1 |
| C(15)–C(16)–C(4) | 122.2 | C(6)–C(7)–C(8) | 114.0 |
| Dihedral Angles, deg | | | |
| S(1)–C(2)–C(3)–C(4) | −4.6 | C(2)–C(10)–C(11)–C(12) | 1.0 |
| C(2)–C(3)–C(4)–S(5) | 1.2 | C(10)–C(11)–C(12)–C(13) | −0.0 |
| C(3)–C(4)–S(5)–C(6) | −84.7 | C(11)–C(12)–C(13)–C(14) | 178.9 |
| C(4)–S(5)–C(6)–C(7) | 59.1 | C(12)–C(13)–C(14)–C(15) | −179.4 |
| S(5)–C(6)–C(7)–C(8) | 54.5 | C(13)–C(14)–C(15)–C(16) | −0.5 |
| C(6)–C(7)–C(8)–S(1) | −57.5 | C(14)–C(15)–C(16)–C(4) | −0.0 |
| C(7)–C(8)–S(1)–C(2) | −51.7 | C(15)–C(16)–C(4)–C(3) | 0.8 |
| C(8)–S(1)–C(2)–C(3) | 83.7 | C(16)–C(4)–C(3)–C(2) | 178.7 |
| C(4)–C(3)–C(2)–C(10) | −179.3 | C(10)–C(2)–S(1)–O(9) | 6.6 |
| C(3)–C(2)–C(10)–C(11) | −1.3 | | |

[a] SCF energy = −1353.5424575 hartrees. Nuclear repulsion energy = 1358.0020788 hartrees. Rotational constant = 0.6172103, 0.4873131, 0.3143144 GHz.

Removing the naphthalene ring in **1–5** and freezing atoms 2–4 would be a severe deviation from the naphthodithiocin system since molecular model studies showed considerable movement of atoms

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(16) Gaussian 86 (Release C) written by Frisch, M.; Binkley, J. S.; Schlegel, H. S.; Roghavachaoi, K.; Martin, R.; Stewart, J. J. P.; Bobrowicz, F.; Defrees, D.; Seeger, R.; Whiteside, R.; Fox, D.; Fluder, E.; and Pople, J. A. Carnegie Mellon University.

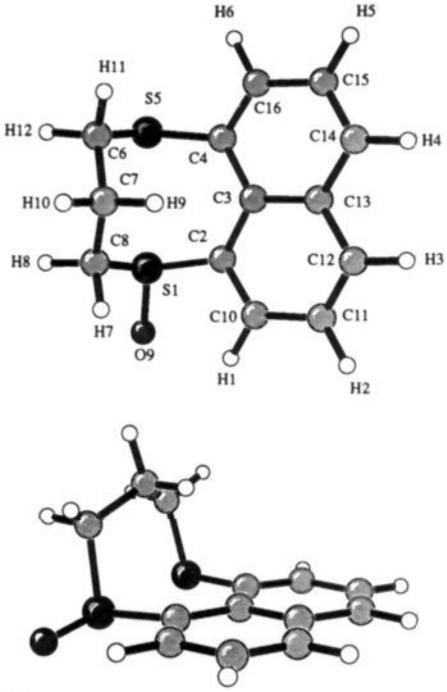

**Figure 2**. Three-dimensional view and labeling scheme for compound **2**.

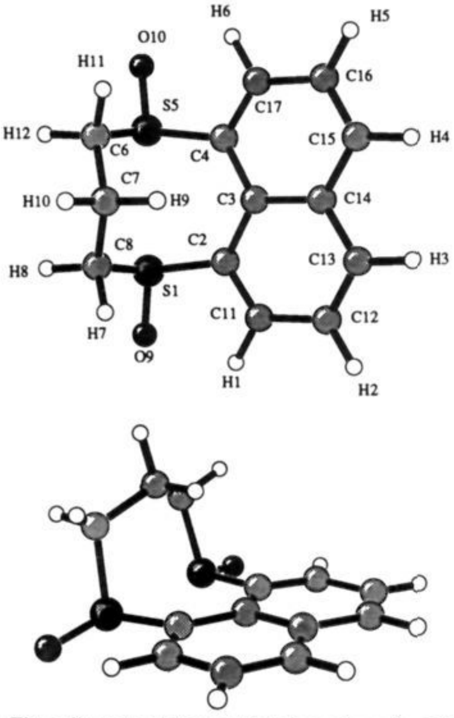

**Figure 3**. Three-dimensional view and labeling scheme for compound **3**.

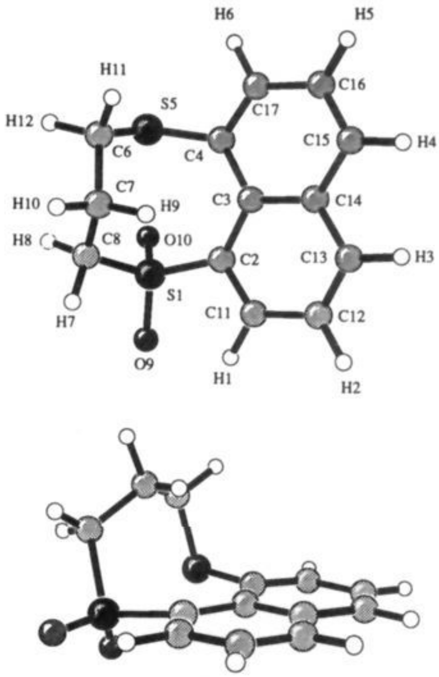

**Figure 4**. Three-dimensional view and labeling scheme for compound **4**.

**Table V**. Optimized Geometry for the Boat Conformer of Compound **3**[a]

| | | | |
|---|---|---|---|
| Interatomic Distances, Å | | | |
| C(2)–C(11) | 1.36 | C(11)–C(12) | 1.42 |
| C(12)–C(13) | 1.35 | C(13)–C(14) | 1.43 |
| C(14)–C(15) | 1.43 | C(15)–C(16) | 1.35 |
| C(16)–C(17) | 1.42 | C(17)–C(4) | 1.36 |
| C(4)–C(3) | 1.45 | C(3)–C(2) | 1.45 |
| C(3)–C(14) | 1.41 | C(2)–S(1) | 1.81 |
| S(1)–O(9) | 1.48 | S(1)–C(8) | 1.83 |
| C(8)–C(7) | 1.54 | C(6)–C(7) | 1.54 |
| S(5)–C(6) | 1.83 | S(5)–O(10) | 1.48 |
| S(1)···S(5) | 3.02 | C(4)–S(5) | 1.81 |
| Interatomic Angles, deg | | | |
| C(2)–C(11)–C(12) | 121.6 | C(8)–C(7)–C(6) | 114.7 |
| C(11)–C(12)–C(13) | 119.4 | C(7)–C(6)–S(5) | 116.8 |
| C(13)–C(14)–C(15) | 119.7 | C(6)–S(5)–C(4) | 96.6 |
| C(13)–C(14)–C(3) | 120.2 | C(6)–S(5)–O(10) | 106.3 |
| C(15)–C(14)–C(3) | 120.2 | O(10)–S(5)–C(4) | 107.2 |
| C(14)–C(15)–C(16) | 121.0 | S(1)–C(2)–C(11) | 114.9 |
| C(15)–C(16)–C(17) | 119.4 | C(3)–C(4)–S(5) | 124.4 |
| C(16)–C(17)–C(4) | 121.6 | C(12)–C(13)–C(14) | 120.9 |
| C(17)–C(4)–S(5) | 114.9 | C(17)–C(4)–C(3) | 120.6 |
| C(8)–S(1)–O(9) | 106.3 | C(4)–C(3)–C(2) | 125.4 |
| C(4)–C(3)–C(14) | 117.3 | C(2)–C(3)–C(14) | 117.3 |
| C(3)–C(2)–C(11) | 120.6 | C(3)–C(2)–S(1) | 124.4 |
| C(2)–S(1)–O(9) | 107.3 | C(2)–S(1)–C(8) | 96.6 |
| C(1)–C(8)–C(7) | 116.8 | | |
| Dihedral Angles, deg | | | |
| S(1)–C(2)–C(3)–C(4) | −3.0 | C(2)–C(11)–C(12)–C(13) | 0.6 |
| C(2)–C(3)–C(4)–S(5) | 3.0 | C(11)–C(12)–C(13)–C(14) | 0.3 |
| C(3)–C(4)–S(5)–C(6) | −83.9 | C(12)–C(13)–C(14)–C(15) | 178.8 |
| C(4)–S(5)–C(6)–C(7) | 55.1 | C(13)–C(14)–C(15)–C(16) | −178.8 |
| S(5)–C(6)–C(7)–C(8) | 56.6 | C(14)–C(15)–C(16)–C(17) | −0.3 |
| C(6)–C(7)–C(8)–S(1) | −56.7 | C(15)–C(16)–C(17)–C(4) | −0.7 |
| C(7)–C(8)–S(1)–C(2) | −54.9 | C(16)–C(17)–C(4)–C(3) | 1.4 |
| C(8)–S(1)–C(2)–C(3) | 83.8 | C(17)–C(4)–C(3)–C(2) | 178.6 |
| C(4)–C(3)–C(2)–C(11) | −178.6 | C(11)–C(2)–S(1)–O(9) | 8.9 |
| C(3)–C(2)–C(11)–C(12) | −1.4 | C(17)–C(4)–S(5)–O(10) | −9.0 |

[a] SCF energy = −1427.37204399 hartrees. Nuclear repulsion energy = 1512.76167166 hartrees. Rotational constant = 0.4911586, 0.4784553, 0.2815090 GHz.

2–4 in this S···S rocking mode. (This was later confirmed by the SCF/STO-3G* calculations.) Any other model of compounds **1**–**5** in which the naphthalene ring was excluded would be too flexible to reasonably approximate **1**–**5**. Thus in order to get meaningful vibrational data for **1**–**5**, it was necessary to perform calculations on the entire molecules. The SCF/STO-3G* equilibrium geometries of **1**–**5**, shown in Figures 1–5 and listed in Tables III–VII, are close to the X-ray structure geometries.[11,12] The calculated S···S nonbonded distance for **1** of 3.05 Å is small compared to the experimental distance of 3.23 Å determined by X-ray crystallography; however, the calculated S···S distances for **2**–**5** of 2.98, 3.02, 3.25, and 3.34 Å, respectively, are very close to the experimental distances of 3.00, 3.05, 3.27, and 3.40 Å, respectively. The calculated angles about the S(1)–O(9) bond are also very close to the experimental angles shown in Table I, since the experimental C(2)–S(1)–O(9) and C(8)–S(1)–O(9) bond angles are within 3° of the corresponding calculated angles and since the experimental S(5)–S(1)–O(9) bond angles are within 5° of the corresponding calculated angles. All other bond dis-

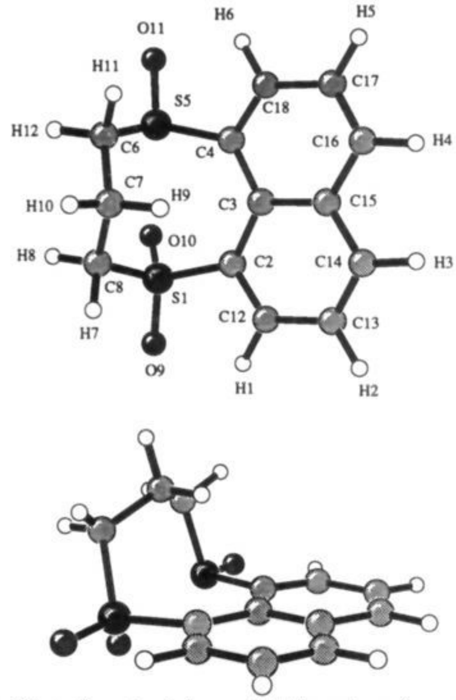

**Figure 5**. Three-dimensional view and labeling scheme for compound **5**.

**Table VI**. Optimized Geometry for the Boat Conformer of Compound **4**[a]

| | | | |
|---|---|---|---|
| Interatomic Distance, Å | | | |
| C(2)–C(11) | 1.36 | C(8)–C(7) | 1.54 |
| C(11)–C(12) | 1.42 | C(7)–C(6) | 1.55 |
| C(12)–C(13) | 1.35 | C(6)–S(5) | 1.78 |
| C(13)–C(14) | 1.43 | S(5)–C(4) | 1.76 |
| C(14)–C(15) | 1.43 | S(1)–O(9) | 1.46 |
| C(15)–C(16) | 1.35 | S(1)–O(10) | 1.46 |
| C(16)–C(17) | 1.42 | S(5)···S(1) | 3.25 |
| C(17)–C(4) | 1.37 | C(4)–C(3) | 1.46 |
| C(3)–C(14) | 1.42 | C(3)–C(2) | 1.46 |
| C(2)–S(1) | 1.82 | S(1)–C(8) | 1.84 |
| Interatomic Angles, deg | | | |
| C(2)–C(11)–C(12) | 122.2 | C(2)–S(1)–O(9) | 106.1 |
| C(11)–C(12)–C(13) | 118.8 | C(2)–S(1)–O(10) | 109.9 |
| C(12)–C(13)–C(14) | 121.1 | C(9)–S(1)–O(10) | 120.3 |
| C(13)–C(14)–C(15) | 118.2 | O(9)–S(1)–C(8) | 104.0 |
| C(14)–C(15)–C(16) | 120.8 | O(10)–S(1)–C(8) | 111.4 |
| C(15)–C(16)–C(17) | 118.9 | C(16)–C(17)–C(4) | 123.0 |
| C(17)–C(4)–C(3) | 119.0 | C(4)–C(3)–C(14) | 117.3 |
| C(2)–C(3)–C(14) | 116.1 | C(3)–C(14)–C(13) | 121.0 |
| C(3)–C(14)–C(15) | 120.8 | C(3)–C(2)–C(11) | 120.6 |
| C(11)–C(2)–S(1) | 111.3 | C(3)–C(2)–S(1) | 127.8 |
| C(2)–S(1)–C(8) | 103.8 | S(1)–C(8)–C(7) | 119.0 |
| C(8)–C(7)–C(6) | 113.8 | C(7)–C(6)–S(5) | 115.1 |
| C(6)–S(5)–C(4) | 99.8 | S(5)–C(4)–C(3) | 125.8 |
| S(5)–C(4)–C(17) | 115.1 | | |
| Dihedral Angles, deg | | | |
| S(1)–C(2)–C(3)–C(4) | −8.9 | C(2)–C(11)–C(12)–C(13) | 1.2 |
| C(2)–C(3)–C(4)–S(5) | −1.2 | C(11)–C(12)–C(13)–C(14) | −1.1 |
| C(3)–C(4)–S(5)–C(6) | −79.2 | C(12)–C(13)–C(14)–C(15) | 179.4 |
| C(4)–S(5)–C(6)–C(7) | 66.4 | C(13)–C(14)–C(15)–C(16) | 179.6 |
| S(5)–C(6)–C(7)–C(8) | 49.5 | C(14)–C(15)–C(16)–C(17) | −1.5 |
| C(6)–C(7)–C(8)–S(1) | −76.5 | C(15)–C(16)–C(17)–C(4) | 1.1 |
| C(7)–C(8)–S(1)–C(2) | −26.9 | C(16)–C(17)–C(4)–C(3) | 1.2 |
| C(8)–S(1)–C(2)–C(3) | 76.0 | C(17)–C(18)–C(4)–C(3) | 1.2 |
| C(4)–C(3)–C(2)–C(11) | 177.4 | C(17)–C(4)–C(3)–C(2) | 177.6 |
| C(3)–C(2)–C(11)–C(12) | 0.4 | C(11)–C(2)–S(1)–O(9) | −0.6 |
| | | C(11)–C(2)–S(1)–O(10) | 130.9 |

[a] SCF energy = −1427.3783685 hartrees. Nuclear repulsion energy = 1527.28618665 hartrees. Rotational constant = 0.5704733, 0.4357817, 0.2931089 GHz.

**Table VII**. Optimized Geometry for the Boat Conformer of Compound **5**[a]

| | | | |
|---|---|---|---|
| Interatomic Distances, Å | | | |
| C(2)–C(12) | 1.36 | C(6)–S(5) | 1.83 |
| C(12)–C(13) | 1.42 | S(5)–C(4) | 1.82 |
| C(13)–C(14) | 1.35 | S(5)–O(11) | 1.48 |
| C(14)–C(15) | 1.43 | S(1)–O(9) | 1.46 |
| C(15)–C(16) | 1.43 | S(1)–O(10) | 1.45 |
| C(16)–C(17) | 1.35 | S(1)···S(5) | 3.34 |
| C(17)–C(18) | 1.42 | C(18)–C(4) | 1.36 |
| C(4)–C(3) | 1.45 | C(3)–C(15) | 1.42 |
| C(3)–C(2) | 1.45 | C(2)–S(1) | 1.82 |
| S(1)–C(8) | 1.84 | C(8)–C(7) | 1.54 |
| C(7)–C(6) | 1.54 | | |
| Interatomic Angles, deg | | | |
| C(2)–C(12)–C(13) | 122.1 | C(7)–C(6)–S(5) | 118.1 |
| C(12)–C(13)–C(14) | 118.7 | C(6)–S(5)–O(11) | 105.1 |
| C(13)–C(14)–C(15) | 121.3 | C(6)–S(5)–C(4) | 96.5 |
| C(14)–C(15)–C(16) | 117.9 | O(11)–S(5)–C(4) | 106.2 |
| C(15)–C(16)–C(17) | 120.9 | S(5)–C(4)–C(3) | 128.1 |
| C(16)–C(17)–C(18) | 118.8 | S(5)–C(4)–C(18) | 111.7 |
| C(17)–C(18)–C(4) | 122.7 | C(18)–C(4)–C(3) | 120.1 |
| C(4)–C(3)–C(2) | 127.7 | C(4)–C(3)–C(15) | 116.5 |
| C(2)–C(3)–C(15) | 115.8 | C(3)–C(15)–C(14) | 121.0 |
| C(3)–C(15)–C(16) | 121.0 | C(3)–C(2)–C(1) | 127.1 |
| C(3)–C(2)–C(12) | 121.0 | C(12)–C(2)–S(1) | 111.8 |
| C(2)–S(1)–O(9) | 106.8 | C(2)–S(1)–O(10) | 109.7 |
| O(9)–S(1)–O(10) | 121.3 | O(9)–S(1)–C(8) | 104.9 |
| O(10)–S(1)–C(8) | 110.1 | S(1)–C(8)–C(7) | 118.1 |
| C(8)–C(7)–C(6) | 115.4 | C(2)–S(1)–C(8) | 102.3 |
| Dihedral Angles, deg | | | |
| S(1)–C(2)–C(3)–C(4) | −4.4 | C(2)–C(12)–C(13)–C(14) | 0.4 |
| C(2)–C(3)–C(4)–S(5) | 3.2 | C(12)–C(13)–C(14)–C(15) | −0.3 |
| C(3)–C(4)–S(5)–C(6) | −79.9 | C(13)–C(14)–C(15)–C(16) | 180.0 |
| C(4)–S(5)–C(6)–C(7) | 54.9 | C(14)–C(15)–C(16)–C(17) | 180.0 |
| S(5)–C(6)–C(7)–C(8) | 57.8 | C(15)–C(16)–C(17)–C(18) | −0.4 |
| C(6)–C(7)–C(8)–S(1) | −70.6 | C(16)–C(17)–C(18)–C(4) | −0.3 |
| C(7)–C(8)–S(1)–C(2) | −38.2 | C(17)–C(18)–C(4)–C(3) | 1.2 |
| C(8)–S(1)–C(2)–C(3) | 75.4 | C(18)–C(4)–C(3)–C(2) | 179.2 |
| C(4)–C(3)–C(2)–C(12) | 179.1 | C(12)–C(2)–S(1)–O(9) | 2.1 |
| C(3)–C(2)–C(12)–C(13) | −0.1 | C(12)–C(2)–S(1)–O(10) | 135.3 |
| | | C(18)–C(4)–S(5)–O(11) | −3.9 |

[a] SCF energy = −1501.20943159 hartrees. Nuclear repulsion energy = 1690.032810934 hartrees. Rotational constant = 0.4558982, 0.4375908, 0.2608296 GHz.

tances, bond angles, and torsional angles for the SCF/STO-3G* geometries are within 0.05 Å, 5°, and 12°, respectively, of the distances and angles for the X-ray structures for **1**–**5**.[17]

The SCF/STO-3G* geometries of **1** and **2** were essentially the same as the SCF/STO-3G geometries calculated earlier,[9] with one significant difference. The STO-3G basis set calculated the S–O bond length in **2** to be 1.79 Å, whereas the S–O bond length was calculated to be 1.48 Å with use of the STO-3G* basis set. Since this distance is 1.50 Å in the X-ray structure[12] of **2**, the STO-3G* basis set is a vast improvement over the STO-3G basis set. Apparently, the d-orbitals in the STO-3G* basis set allow for polarization of the S–O bond, which is necessary to accurately describe this bond.[18] The SCF/STO-3G* S–O bond lengths of **3**–**5** were also in accord with the bond lengths found by X-ray crystallography,[12] since S–O bond lengths as determined by the SCF/STO-3G* calculations or by X-ray crystallography are within 0.04 Å.

The vibrational modes for compounds **1**–**5** are listed in Tables VIII–XII. The magnitudes of the frequencies of the vibrational modes are always overestimated when the STO-3G* basis set is used.[19] To correct for this error, all frequencies were scaled by a factor of 0.79.[20] Generally, the scaled frequencies and the

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[17] The X-ray structure of **1** revealed that it exists in a chair conformation in the crystalline state. Since the STO-3G* calculations were carried our on **1** in the boat conformation, the dihedral angles were very different for the X-ray and STO-3G* geometries. The bond angles and bond distances, however, were still close to the same value for the STO-3G* and X-ray geometries.

[18] Collins, J. B.; Schleyer, P. v. R.; Binkley, J. S.; Pople, A. *J. Chem. Phys.* **1964**, *64*, 5142. Collins, M. P. S.; Duke, B. J. *Chem. Phys. Lett.* **1976**, *42*, 364. Roos, B.; Siegbahn, P. *Theor. Chim. Acta (Berlin)* **1971**, *21*, 368.

[19] Hess, B. A., Jr.; Schaad, L. J. *Chem. Rev.* **1966**, *86*, 713.

**Table VIII.** STO-3G* Calculated Vibrational Modes for the Boat Conformer of Compound **1**

| mode no.[a] | approximate description[b] | predicted wavenumbers, cm$^{-1}$ | | tentative assignment, cm$^{-1}$ |
|---|---|---|---|---|
| | | unscaled | scaled[c] | |
| 1 | S—S rock | 54 | 43 (0.03) | |
| 26 | ArC—H out-of-plane be | 931 | 735 (36.9) | 760 (100.0) |
| 29 | ArC—H out-of-plane be | 988 | 780 (26.3) | 819 (94.8) |
| 61 | C═C st | 1894 | 1496 (3.2) | 1544 (46.4) |
| 62 | C═C st | 1942 | 1534 (21.3) | 1591 (47.4) |
| 64 | C—H st | 3563 | 2815 (10.4) | 2850 (20.0) |
| 69 | C—H st | 3709 | 2930 (23.8) | 2911 (68.7) |
| 72 | C—H st | 3722 | 2940 (54.6) | 2931 (48.0) |
| 74 | C—H st | 3742 | 2956 (18.5) | 2956 (28.0) |

[a] Seventy-five vibronic modes were found. The modes shown here are the prominent C—H stretching, C═C stretching, and aromatic C—H out-of-plane bending, in addition to the S—S rocking mode. [b] be = bend; st = stretch; rock = rocking; numbers in parentheses are relative intensities. [c] The calculated highest C-H stretch was scaled so that it equaled the experimental C-H stretch band. This scalar of 0.79 was then used to scale all the other frequencies.

**Table IX.** STO-3G* Calculated Vibrational Modes for the Boat Conformer of Compound **2**

| mode no.[a] | approximate description[b] | predicted wavenumbers, cm$^{-1}$ | | tentative assignment, cm$^{-1}$ |
|---|---|---|---|---|
| | | unscaled | scaled[c] | |
| 1 | S—S rock | 58 | 46 (0.6) | |
| 28 | ArC—H out-of-plane be | 929 | 733 (25.1) | 766 (76.3) |
| 30 | ArC—H out-of-plane be | 988 | 780 (25.8) | 825 (76.3) |
| 46 | S—O st | 1365 | 1078 (30.0) | 1008 (100.0) |
| 47 | S—O st | 1372 | 1084 (100.0) | 1024 (98.3) |
| 65 | C═C st | 1940 | 1532 (22.3) | 1591 (32.2) |
| 72 | C—H st | 3709 | 2930 (16.2) | 2903 (69.5) |
| 74 | C—H st | 3721 | 2940 (58.0) | 2923 (81.4) |
| 75 | C—H st | 3722 | 2940 (21.9) | 2942 (69.5) |
| 77 | C—H st | 3741 | 2955 (12.7) | 2952 (50.0) |
| 78 | C—H st | 3741 | 2955 (11.2) | 2962 (25.0) |

[a] Seventy-eight vibronic modes were found. The modes shown here are the prominent C—H stretching, C═C stretching, aromatic C—H out-of-plane bending, and S—O stretching modes, in addition to the S—S rocking mode. [b] be = bend; st = stretch; rock = rocking; numbers in parentheses are relative intensities. [c] The calculated highest C-H stretch in compound **1** was scaled so that it equaled the experimental C-H stretch band. This scalar of 0.79 was then used to scale all the other frequencies for all other compounds.

**Table X.** STO-3G* Calculated Vibrational Modes for the Boat Conformer of Compound **3**

| mode no.[a] | approximate description[b] | predicted wavenumbers, cm$^{-1}$ | | tentative assignment, cm$^{-1}$ |
|---|---|---|---|---|
| | | unscaled | scaled[c] | |
| 1 | S—S rock | 58 | 46 (0.04) | |
| 30 | ArC—H out-of-plane be | 925 | 731 (28.1) | 758 (53.6) |
| 32 | ArC—H out-of-plane be | 989 | 781 (36.2) | 815 (60.7) |
| 48 | S—O st | 1363 | 1077 (78.0) | 1001 (52.9) |
| 49 | S—O st | 1369 | 1082 (82.3) | 1040 (100.0) |
| 50 | S—O st | 1371 | 1083 (88.1) | 1050 (82.1) |
| 68 | C═C st | 1941 | 1533 (10.6) | 1590 (8.7) |
| 76 | C—H st | 3713 | 2933 (13.9) | 2890 (3.5) |
| 77 | C—H st | 3722 | 2940 (100.0) | 2907 (7.1) |
| 80 | C—H st | 3742 | 2956 (27.1) | 2948 (15.7) |

[a] Eighty-one vibronic modes were found. The modes shown here are the prominent C—H stretching, C═C stretching, aromatic C—H out-of-plane bending, and S—O stretching modes, in addition to the S—S rocking mode. [b] be = bend; st = stretch; rock = rocking; numbers in parentheses are relative intensities. [c] The calculated highest C-H stretch in compound **1** was scaled so that it equaled the experimental C-H stretch band. This scalar of 0.79 was then used to scale all the other frequencies for all other compounds.

**Table XI.** STO-3G* Calculated Vibrational Modes for the Boat Conformer of Compound **4**

| mode no.[a] | approximate description[b] | predicted wavenumbers, cm$^{-1}$ | | tentative assignment, cm$^{-1}$ |
|---|---|---|---|---|
| | | unscaled | scaled[c] | |
| 1 | S—S rock | 46 | 36 (0.6) | |
| 30 | ArC—H out-of-plane be | 926 | 731 (31.9) | 743 (76.7) |
| 32 | ArC—H out-of-plane be | 991 | 783 (12.2) | 761 (87.5) |
| 46 | S—O st | 1318 | 1042 (73.4) | 1107 (93.3) |
| 47 | S—O st | 1341 | 1059 (44.3) | 1121 (100.0) |
| 58 | S—O st | 1605 | 1268 (27.7) | 1267 (70.8) |
| 59 | S—O st | 1615 | 1276 (100.0) | 1288 (100.0) |
| 68 | C═C st | 1940 | 1533 (11.1) | 1493 (45.8) |
| 69 | C═C st | 1950 | 1541 (20.6) | 1595 (21.7) |
| 74 | C—H st | 3713 | 2933 (13.0) | 2900 (4.1) |
| 77 | C—H st | 3725 | 2942 (21.5) | 2914 (12.5) |
| 79 | C—H st | 3733 | 2950 (38.4) | 2924 (16.7) |
| 80 | C—H st | 3744 | 2958 (11.5) | 2934 (14.2) |
| 81 | C—H st | 3747 | 2959 (24.7) | 2974 (5.8) |

[a] Eight-one vibronic modes were found. The modes shown here are the prominent C—H stretching, C═C stretching, aromatic C—H out-of-plane bending, and S—O stretching modes, in addition to the S—S rocking mode. [b] be = bend; st = stretch; rock = rocking; numbers in parentheses are relative intensities. [c] The calculated highest C-H stretch in compound **1** was scaled so that it equaled the experimental C-H stretch band. This scalar of 0.79 was then used to scale all the other frequencies for all other compounds.

experimental frequencies are in good agreement for compounds **1–5**. In particular the calculated (scaled) C—H stretches, C═C stretches, and aromatic C—H out-of-plane stretches are within 60 cm$^{-1}$ of the experimental frequencies. In addition, the calculated S–O stretching frequencies for compounds **2–5** are within 70 cm$^{-1}$ of the experimental frequencies. This is a significant improvement over the SCF/STO-3G calculated S–O stretching frequencies[9] which ranged from 440 to 470 cm$^{-1}$ (experimental = 1008, 1024 cm$^{-1}$). This improvement is due to the more accurate description of the S–O bond using the STO-3G* basis set over the STO-3G basis set, as was described earlier.

## Discussion

The most interesting vibrational mode for our study is the S–S rocking mode. This mode has been described elsewhere[9] and is essentially the mode used to flip from one boat conformation to the other boat conformation as is shown in Figure 6. The important feature of the S–S rocking mode is the S···S distance, which increases throughout the course of this mode. In fact, AM1 calculations have shown that the S···S distance must increase by 0.9 Å in order to complete the ring flip.[12] This S···S rocking mode should then make an excellent probe of the strength of the S···S transannular interactions of compounds **1–5**. If an attractive S···S interaction exists in **2–5** versus **1** then the frequency of the S–S rocking mode should be higher in **2–5** versus **1**, and the strength of this attractive interaction should be proportional to the magnitude of this increase.

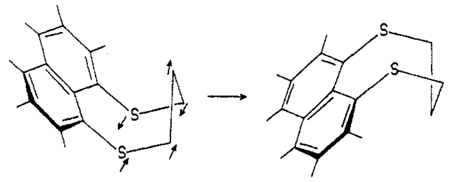

**Figure 6.** Ring flip in compound **1** via the S–S rocking mode.

The first vibrational mode (lowest frequency) for **1** is shown in Figure 7. The first drawing in the figure shows the equilibrium geometry of the molecule while the second and the third drawings show the position of the atoms after applying the first mode of

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(20) The factor 0.79 was chosen so that the highest calculated C–H frequency for **1** would equal the highest experimental C–H frequency.

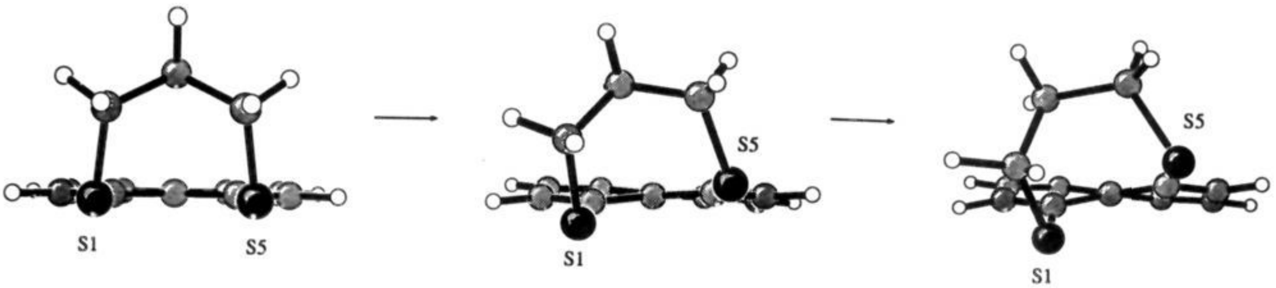

**Figure 7**. Progression of the first vibrational mode for compound **1**.

**Table XII**. STO-3G* Calculated Vibrational Modes for the Boat Conformer of Compound **5**

| mode no.[a] | approximate description[b] | predicted wavenumbers, $cm^{-1}$ unscaled | predicted wavenumbers, $cm^{-1}$ scaled[c] | tentative assignment, $cm^{-1}$ |
|---|---|---|---|---|
| 1 | S—S rock | 30 | 24 (0.3) | |
| 31 | ArC—H out-of-plane be | 920 | 726 (12.6) | 759 (66.7) |
| 34 | ArC—H out-of-plane be | 993 | 785 (11.7) | 832 (43.3) |
| 48 | S—O st | 1314 | 1038 (29.3) | 1008 (58.3) |
| 49 | S—O st | 1337 | 1056 (46.2) | 1040 (83.3) |
| 50 | S—O st | 1354 | 1070 (41.5) | 1120 (80.8) |
| 52 | S—O st | 1370 | 1082 (49.3) | 1131 (79.2) |
| 62 | S—O st | 1625 | 1283 (78.1) | 1302 (100.0) |
| 70 | C=C st | 1890 | 1493 (6.3) | 1500 (29.2) |
| 71 | C=C st | 1942 | 1534 (8.6) | 1558 (12.5) |
| 72 | C=C st | 1951 | 1541 (7.1) | 1598 (25.0) |
| 77 | C—H st | 3709 | 2930 (13.1) | 2918 (15.8) |
| 80 | C—H st | 3722 | 2940 (38.6) | 2938 (12.5) |
| 82 | C—H st | 3733 | 2949 (32.2) | 2948 (12.5) |
| 84 | C—H st | 3748 | 2961 (20.0) | 2958 (12.5) |

[a] Eight-four vibronic modes were found. The modes shown here are the prominent C—H stretching, C=C stretching, aromatic C—H in-plane bending, and S—O stretching modes, in addition to the S—S rocking mode. [b] be = bend; st = stretch; rock = rocking; numbers in parentheses are relative intensities. [c] The calculated highest C-H stretch in compound **1** was scaled so that it equaled the experimental C-H stretch band. This scalar of 0.79 was then used to scale all the other frequencies for all other compounds.

**Table XIII**. Ajusted Frequencies[a] for the S···S Rocking Mode for Compounds **1–5**

| compd | unadjusted freq, $cm^{-1}$ | mass of 8-membered ring, g | adjusted freq,[a] $cm^{-1}$ |
|---|---|---|---|
| **1** | 43 | 142 | 43 |
| **2** | 46 | 158 | 49 |
| **3** | 46 | 174 | 51 |
| **4** | 36 | 190 | 42 |
| **5** | 24 | 206 | 29 |

[a] Adjusted frequency = unadjusted frequency $(x/142)^{1/2}$, where $x$ is the sum of the masses of atoms in the eight-membered ring.

vibration. The first vibrational mode for compounds **2–5** is analogous to that of **1**. Clearly the first or lowest vibrational mode for compounds **1–5** is the S–S rocking mode. *¹H NMR* spectroscopy studies on the ring flipping of **1–5** support the low magnitude of these frequencies.[12]

The sum of the mass of the atoms involved in the S···S rocking mode increases going from **1** to **5** due to the addition of oxygen atoms. This increase in mass will lower the frequency of the S···S rocking mode. This decrease is approximately proportional to $(m_1/m_2)^{1/2}$ where $m_1$ is the mass of the smaller molecule and $m_2$ is the mass of the larger molecule. In order to relate the magnitude of the frequency of the S···S rocking mode to the strength of the S···S interaction, the increase in mass must be factored out. Since most of the S···S rocking mode is localized in the eight-membered ring, multiplying the magnitude of the frequency by $(x/142)^{1/2}$ ($x$ is the sum of the masses of atoms in the eight-membered ring) will approximately account for the increase in mass from **1** to **5**. Table XIII shows the adjusted frequencies for the S···S rocking mode for **1–5**.

**4** (42 $cm^{-1}$) and **5** (29 $cm^{-1}$) have a lower adjusted frequency for the S–S rocking mode than **1** (43 $cm^{-1}$). Thus, the SCF/STO-3G* calculations predict no attractive transannular interaction exists in **4–5** relative to **1**. This is in agreement with the analysis of the X-ray structures of **1** and **4–5** discussed earlier, where it was found that no attractive interaction was present based on the long S···S distances in **4** and **5**.

**2** (49 $cm^{-1}$) and **3** (51 $cm^{-1}$) have a slightly higher adjusted frequency for the S–S rocking mode than **1** (43 $cm^{-1}$). Thus, the calculations would predict a small attractive S···S transannular interaction is present in **2–3** relative to **1**. It should be noted that presumably there is no attractive interaction between the sulfur atoms in **1**. For 1,5 S···O nonbonded interaction an electronegative fluorine atom attached to sulfur and cis conjugation are necessary for significant S···O interaction.[21] With carbon ($sp^3$) attached to sulfur instead of fluorine there is no significant S···O attractive interaction.[22] This also is in agreement with the X-ray structure analysis of **1–3** where it was found that an attractive S···S interaction exists in **2** and **3** based on the short S···S distances and apparent rehybridization of the sulfoxide sulfur in **2** and **3**. However, the STO-3G* calculations show that the strength of the attractive transannular interaction in **2–3** is very weak. The weak attraction may be due to dipole–dipole or charge-transfer interactions, but the calculations show no significant S···S bond formation. It has suggested[23] previously that d-orbitals are essential for S···O nonbonded interaction and that d-orbitals may be used up in sulfoxide S=O bonding precluding their ability to participate in covalent S···O interaction. A similar explanation may be the reason for a lack of significant S···S bond formation in **2** and **3**.

The X-ray analysis of **1–3** showed the same characteristics for transannular interaction that other authors have ascribed to incipient bond formation.[4] But since our calculations have ruled out significant S···S bond formation in **2–3**, we believe this illustrates the danger of inferring bond formation in nonbonded contacts based on intramolecular distances and small angle distortions about the interacting atoms.

The present analysis is based on calculating the harmonic frequencies. Such an approach is always subject to inaccuracies especially when one deals with a sizable anharmonic contribution in the vibrational mode under consideration. In order to verify the reliability of the harmonic approximation for the S–S rocking mode, we performed single-point SCF/STO-3G* calculations for molecule **1** at six phases of the vibration. The first three phases corresponded to the structures obtained by adding the Cartesian coordinates representing the mode with coefficients $d = 0.1, 0.2$, and 0.3 to the equilibrium geometry. For the last three phases we used negative values of the displacement coefficient, $d$, equal to −0.1, −0.2, and −0.3. In the next step a fourth-degree polynomial of the form

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$$E(d) = E_e + \tfrac{1}{2}kd^2 + k'd^3 + k''d^4 \qquad (2)$$

was used to produce a fit to the energy as a function of the displacement parameter. In eq 2 $E_e$ represents the value of the energy at the minimum and $k$ is equal to the harmonic force constant. The values of the asymmetric and symmetric anharmonic force constants, $k'$ and $k''$ (the only two variables in eq 2), were found by minimizing the least-squares difference between the calculated energies and the corresponding values of the polynomial (**2**). The minimization procedure produced the following form of the energy as a function of the displacement parameter (energy in atomic units):

$$E(d) = (-1279.7062231) + \tfrac{1}{2}(0.0018430)d^2 + (-0.0000274)d^3 + (0.0009394)d^4 \qquad (3)$$

Next we estimated how much the anharmonic contribution in eq 3 would alter the value of the harmonic frequency. Our estimate was based on calculating the energy spectrum of the anharmonic oscillator in the potential of eq 3. Upon comparison of the harmonic and anharmonic energies for the fundamental excitation, equal to 55 and 59 cm$^{-1}$, respectively, we conclude that the harmonic approximation should be quite reliable in examining the S–S rocking motion.

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**Supplementary Material Available:** Tables of Cartesian coordinates for the optimized geometry of compounds **1**–**5** (5 pages). Ordering information is given on any current masthead page. Complete lists of the calculated vibrational modes for compounds **1**–**5** are available from the authors at the BITNET address LUDWIK@RVAX.CCIT.ARIZONA.EDU.

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# Charge Development at the Transition State: A Second-Order Møller–Plesset Perturbation Study of Gas-Phase $S_N2$ Reactions

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**Abstract:** A systematic analysis of the charge distribution at the transition state has been carried out for the model $S_N2$ reactions $N^- + CH_3X \rightarrow CH_3N + X^-$, where X = H, $NH_2$, OH, F, CCH, $\underline{C}N$, $\underline{N}C$, SH, and Cl for N = H and X = H, $NH_2$, OH, F, $\underline{C}N$, SH, and Cl for N = F. Second-order Møller–Plesset perturbation calculations indicate that for some, but not all, reactions the charges on the nucleophile and leaving group at the transition state are equal. In such cases the assumption that the transition state occurs in the vicinity of the crossing point of valence bond configurations $\psi_1$ and $\psi_2$ holds. However, in general, the contributions of the reactant and product wave functions to the transition state are not equal. With an electronegative nucleophile or leaving group, charge development on the nucleophile or leaving group at the transition state is small. A large contribution of the $N;^-R{:}X^-$ configuration (in addition to its contribution to the reactant and product) to the transition state leads to large charge development at the transition state. All other factors being equal, a more exothermic reaction leads to less charge development at the transition state. Also the charge distributions calculated at different theoretical levels (with and without electron correlation) are compared.

## Introduction

Charge development at the transition state (TS) is central to chemistry because most reactions involve electron transfer in the transition state. An understanding of charge development at the transition state enhances our ability to predict reaction rates and to rationalize reaction mechanisms. Unfortunately, a direct study of the TS charge distribution is not a trivial problem. From a theoretical perspective it requires a proper definition of atoms in molecules, while experimentally, the charge distribution in the transition state is studied indirectly by the effects of substituents on the rate.[1]

Two completely different predictions about the TS charge distribution have appeared in the literature. The first one comes from the famous Leffler–Hammond postulate[2] which states that TS properties are related to the position of the TS along the reaction coordinate. An early TS is expected to have a reactant-like charge distribution and a later TS is predicted to have a product-like charge distribution. The other prediction comes from Shaik and Pross's valence bond configuration mixing model.[3] According to Shaik and Pross, the charge distribution at the TS is a special property and is unrelated to the position of the TS along the reaction coordinate. For simple $S_N2$ reactions, they predict that the charges on the entering nucleophile and leaving group are equal and that the charges do not differ from one reaction to another.[3c]

In order to understand the transition-state charge distribution and its relationship with the position of the TS along the reaction coordinate, we have carried out studies of the TS charge distribution for model $S_N2$ reactions. We use the charge partition method due to Bader and co-workers,[4] according to which, an atom in a molecule is defined as a real space surrounded by a zero-flux surface. The charge on an atom is obtained by subtracting the total number of electrons over the atomic basin from its nuclear

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