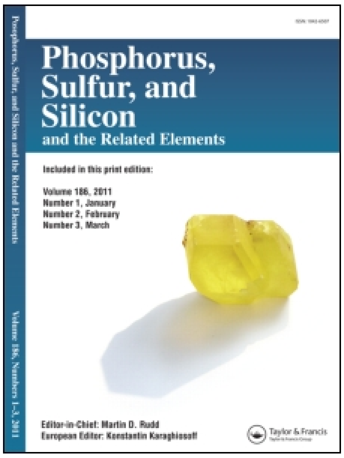

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Density Functional Calculations on Homonuclear Polysulfur Ring Molecules, S_5-S_{16}

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The density functional method, B3PW91, using the 6–311+G(3df) basis function set from the *Gaussian 98* collection of programs, was used to successfully reproduce the experimental structure parameters of polysulfur ring molecules, $S_6 - S_{14}$. Structural predictions of S_5, S_{15}, and S_{16} are also given. The relative electronic energies are also compared.

Keywords: Elemental Sulfur; Molecular Rings; Density Functional Theory

Introduction. The diverse structural chemistry of compounds containing sulfur-sulfur bonds is well established[1]. Nominal S-S single bond lengths run in the range of 189 to 239 pm, so these chemical species offer a substantial theoretical challenge. A subset of this collection are the homonuclear polysulfur ring molecules, many of which have been structurally characterized[2]. Even within this homologous group there is considerable bonding diversity, and therefore, they serve as excellent models to test theoretical methods. Theoretical studies of many of these molecules have been undertaken with mixed results. In recent years, density functional techniques have been applied successfully to many systems, especially in organic chemistry[3], and with rapid advances in computer hardware and quantum chemistry software, the theoretical studies of ever larger systems are becoming increasingly accessible. Here we report the successful application of density functional calculations to the structures of the series of polysulfur ring molecules S_5 through S_{16}.

Calculations. Series of calculations were carried out using the *Gaussian 98*[4] system of programs. Geometry optimized calculations using a variety of methods and basis function sets was used on test compounds. The best results were produced using the hybrid density functional method, B3PW91, which uses the Becke three parameter exchange functional and the Perdew-Wang correlation functional, and the triple zeta basis set, 6-311+G(3df), which includes both diffuse and polarization functions. The polarization functions proved to have much greater effects on the results than the diffuse functions.

Results and Discussion. Table 1. shows the structural parameter results of the calculations and compares them with average experimental data. The experimental data and molecular topologies and described elsewhere[2]. There are no experimental data for S_5, so this is a predicted structure, similar to the work of others.

Table 1. Calc vs. Exp Idealized Structural Parameters of Sn Rings

Ring Sn n =	5		6		7		8		9	
Symmetry	Cs		D3d		Cs		D4d		C2	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
Bond Lengths (pm)	207.6		206.4	206.8	204.7	204.9	205.6	205.0	206.3	205.6
	201.9				210.5	210.2			204.2	203.8
	218.9				198.6	199.6			207.8	206.7
					219.3	218.1			205.3	204.9
									206.4	205.3
Bond Angles (deg)	90.4		102.9	102.6	107.0	106.1	108.8	108.2	104.4	103.7
	99.9				102.8	102.3			110.8	109.4
	100.9				107.0	106.3			108.7	107.4
					108.3	107.1			107.4	105.7
									108.8	108.2
Dihed. Angles (deg)	63.4		73.4	73.8	76.8	76.2	97.8	98.5	-74.7	-76.7
	39.9				105.4	107.4			61.9	62.3
	0.0				81.9	84.0			-113.2	-114.2
					0.0	1.3			86.3	86.8
									76.0	75.4

……

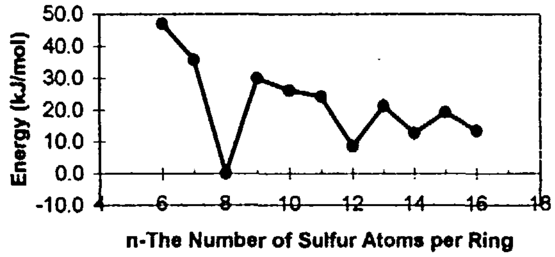
Ring Sn n =	10		11		12		13		14	
Symmetry	D2		C2		D3d		C2		Cs	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
Bond Lengths (pm)	205.1	204.9	205.7	204.6	205.8	205.2	205.8	205.1	206.6	205.3
	207.6	207.4	205.9	206.4			205.8	205.4	205.7	205.2
	203.9	203.6	205.0	204.6			206.3	205.9	205.9	206.0
			207.4	206.4			204.9	204.4	206.2	205.1
			203.9	203.7			208.4	207.3	205.4	205.1
			209.5	211.0			201.5	201.6	206.1	205.8
							211.9	211.3	205.7	204.8
Bond Angles (deg)	112.7	110.2	104.4	103.8	107.7	106.6	109.8	107.8	109.4	108.4
	105.7	103.5	107.5	104.6	108.4		109.4	106.8	109.3	107.8
	107.4	107.1	108.7	106.4			108.0	106.1	106.3	104.8
			109.1	107.0			106.1	105.2	106.2	104.2
			110.5	107.6			103.6	103.0	106.1	105.0
			109.3	106.4			110.5	107.3	110.0	107.7
							110.0	107.2	109.8	106.5
									110.2	109.3
Dihed. Angles (deg)	-78.5	-78.6	89.2	91.8	87.4	88.0	-88.3	-87.0	92.4	95.3
	121.7	122.6	-72.4	-71.2			95.1	95.6	80.8	76.2
	-76.7	-76.1	-82.2	-81.9			79.0	78.4	-100.6	-101.1
			116.5	116.2			-89.1	91.4	-101.3	-98.3
			-103.0	-104.0			-110.6	112.6	82.7	79.3
			133.9	140.5			77.5	75.4	99.4	103.9
							32.5	29.5	-106.5	-98.3

In most cases, the calculated bond length results are within 1 pm and the angular results are within 2 degrees, which is excellent. This gives us confidence in the calculated results for S_{15} and S_{16}, whose structures have not been experimentally determined. The optimized structural parameters are as follows for S_{15} (C_2 symmetry) : bond lengths (pm) [R(1,2) & R(1,15)=206.5; R(2,3) & R(14,15)=205.9; R(3,4) & R(13,14)=205.9; R(4,5) & R(12,13)=206.2; R(5,6) & R(11,12)=205.5; R(6,7) & R(10,11)=206.1; R(7,8) & R(9,10)=205.3; R(8,9)=206.6], bond angles (°) [A(2,1,15)=109.1; A(1,2,3) & A(14,15,1)=105.5; A(2,3,4) & A(13,14,15)=109.4; A(3,4,5) & A(12,13,14)=108.6; A(4,5,6) & A(11,12,13)=109.4; A(5,6,7) & A(10,11,12)=108.4; A(6,7,8) & A(9,10,11)=104.1; A(7,8,9) & A(8,9,10)=107.2], dihedral angles (°) [D(15,1,2,3) & D(14,15,1,2)=107.1;

D(1,2,3,4) & D(13,14,15,1)= -93.7; D(2,3,4,5) & D(12,13,14,15)= -101.5; D(3,4,5,6) & D(11,12,13,14)=81.3; D(4,5,6,7) & D(10,11,12,13)=77.1; D(5,6,7,8) & D(9,10,11,12)= -83.4; D(6,7,8,9) & D(9,10,11,12)= -79.3; D(7,8,9,10)= -112.3]. The calculated molecular S_{16} D_{4d} has a structure similar to that of S_{12}, there are three parallel planes of atoms in a 4, 8, 4 configuration. All S-S bond are equivalent with lengths of 205.8 pm. There are two bond angles: 109.9° for those centered on atoms in the middle plane and 105.8° for the others. All dihedral angles are 98.8° or -98.8°.

Finally, the calculated relative electronic energies normalized to S_8 are represented in Figure 1 . We believe that the quantitative values are not correct, but the relative positions are.

Figure 1. Relative Electronic Energy of Sn Rings



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