Inorganica Chimica Acta, *181* (1991) 81–83

Electronic structure of S_2F_{10}

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(Received June 20, 1990; revised October 4, 1990)

Abstract

The electronic structure of S_2F_{10} has been studied by semi-empirical and *ab initio* MO methods. Both S_2F_{10} conformers: staggered (D_{4d} symmetry) and eclipsed (D_{4h} symmetry) show a very similar electronic structure which can be rationalized in terms of an SF_6 dimer.

Introduction

Disulfur decafluoride (S_2F_{10}) is a compound often produced during electrical discharges in SF_6 insulator gas (dielectric breakdown). Very little work has been reported concerning its electronic structure [1, 2]. The results obtained with the CNDO/2 method were solely concerned with conformational analysis and prediction of electronic transition energies. We wish to present here a more detailed analysis of the title molecule and some of its properties using semi-empirical and *ab initio* MO calculations.

Computational details

The calculations were done using AMPAC and Gaussian 86 programme packages. Accurate experimentally determined geometry [3] was used in the input for the calculations on staggered and eclipsed conformers (D_{4d} and D_{4h} symmetries, respectively).

The measured S_2F_{10} geometry parameters were: $S–S = 227.45$ pm, $S–F_e = 157.43$ pm, $S–F_a = 154.76$ pm, $< F_eSF_a = 89.81°$ where e, a subscripts refer to equatorial and axial fluorine atoms, respectively.

Semi-empirical calculation used AM1 Hamiltonian and its purpose was to provide enthalpies of formation which are much more expensive to compute with the *ab initio* method. In view of the molecule's size we employed the 3-21G* basis set (polarization functions on S atoms only) in the *ab initio* calculation. The single point calculation with this set represented a compromise between computational cost and virtual memory requirements. No attempt was made to describe electron correlation because it would not be meaningful at 3-21G* level.

Results and discussion

S_2F_{10} can exist in two important conformations: staggered and eclipsed. To facilitate the description of its electronic structure we have summarized the orbital symmetries in Table 1.

The gas phase electron diffraction data favoured staggered conformation with small internal rotation barrier. The estimated heights of the barrier were 10.04 and 13.39 kJ mol^{-1} [3]. Both values appeared lower than the CNDO/2 result [1]. Barrier height obtained in this work using the AM1 method was found to be 9.62 kJ mol^{-1} which agrees with the results above. Electron diffraction study [3] also showed that axial bonds were 2.76 pm shorter than equatorial bonds.

A description of the electronic structure of S_2F_{10} and some of its properties is given in Tables 2 and 3.

The title molecule can intuitively be considered an SF_6 dimer and thus the comparison with the SF_6 electronic structure may be established (Fig. 1). The energy level diagram shows considerable similarity between the electronic structures of SF_6 [4] and S_2F_{10}. The main difference is the presence of a low binding energy HOMO orbital in S_2F_{10} which is an S–S bonding σ orbital. Other orbitals in the 15–24 eV energy region correspond to various S–F bonding and non-bonding (F 2p) lone pair orbitals (n_F). An indication of the correctness of a simple dimer picture of S_2F_{10} can be obtained by considering the splitting of S–F bonding orbitals as the symmetry is lowered from O_h to D_{4h}. S–F bonding orbitals $5t_{1u}$ and $4t_{1u}$ in SF_6 correlate (on the basis of symmetry) with a_{2u} and e_u orbitals in S_2F_{10}. The S_2F_{10} orbitals mentioned should therefore also have a pronounced bonding character; an argument confirmed by *ab initio* results.

0020-1693/91/$3.50

TABLE 1. MO symmetry species of S_2F_{10}

	D_{4d} (staggered)	D_{4h} (eclipsed)
σ-orbitals	$3a_1 + 2b_2 + e_1 + e_2 + e_3$	$3a_{1g} + b_{1g} + e_g + 2a_{2u} + b_{2u} + e_u$
π-orbitals	$a_1 + a_2 + b_1 + b_2 + 3e_1$ $2e_2 + 3e_3$	$a_{1g} + a_{2g} + b_{1g} + b_{2g} + 3e_g + a_{1u}$ $a_{1u} + a_{2u} + b_{1u} + b_{2u} + 3e_u$
n_F (axial)	$e_1 + e_3$	$e_g + e_u$
SF (axial)	$a_1 + b_2$	$a_{1g} + a_{2u}$

TABLE 2. SCF valence orbital energies ($-\epsilon_{SCF}$) and MO characters for S_2F_{10}

D_{4d}		D_{4h}	
MO	$-\epsilon_{SCF}$ (eV)	MO	$-\epsilon_{SCF}$ (eV)
a_1(SS)	14.67	a_{1g}(SS)	14.70
a_2(n_F)	18.23	e_g(n_F)	18.08
e_3(n_F)	18.38	a_{1u}(n_F)	18.18
b_1(n_F)	18.48	a_{2g}(n_F)	18.44
b_2(SF)	18.89	b_{2u}(n_F)	18.53
e_1(n_F)	18.94	a_{2u}(SF)	18.57
e_1(n_F)	19.21	e_u(n_F)	19.07
e_3(n_F/S 3d)	19.42	e_g(n_F)	19.10
e_2(SF/S 3d)	19.42	b_{2u}(SF/S 3d)	19.23
e_2(n_F)	19.50	e_u(n_F)	19.43
a_1(SF)	19.70	b_{1g}(SF/S 3d)	19.53
e_3(n_F)	21.01	a_{1g}(SF)	19.85
e_1(n_F)	22.03	b_{1g}(n_F)	20.46
e_2(n_F)	22.17	e_g(n_F)	20.91
b_2(SF)	22.69	b_{1u}(n_F)	21.88
e_3(SF)	24.42	e_u(n_F)	22.15
e_1(SF)	24.51	b_{2g}(n_F)	22.28
a_1(SF)	25.77	a_{2u}(SF)	22.64
b_2(S 3s)	28.91	e_g(SF)	24.18
a_1(S 3s)	30.74	e_u(SF)	24.66
e_2(F 2s)	44.9	a_{1g}(SF)	25.80
		a_{2u}(S 3s)	28.81
		a_{1g}(S 3s)	30.80
		b_{2u}(F 2s)	44.7

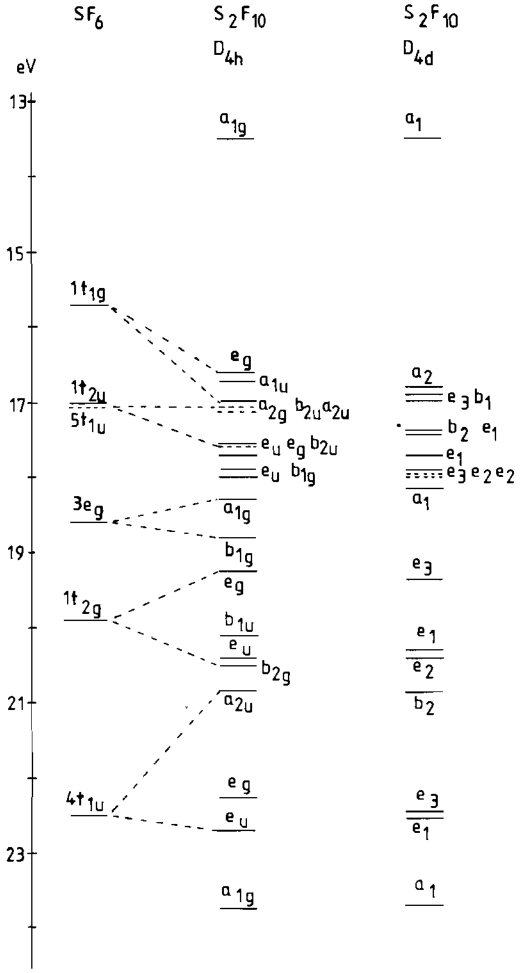

Fig. 1. Energy level diagram for SF_6 and S_2F_{10}.

Similar reasoning can be applied to other orbitals and the results are shown in Fig. 1. The D_{4d} point group is not a subgroup of D_{4h} hence no correlation based on symmetry arguments alone can be established, nonetheless orbital energies of the two conformers do point out a similarity between the electronic structures.

Mulliken population analysis (Table 3) provides further insight into the bonding.

Since meaningful comparisons can only be made within the same basis set used we have for that purpose also performed *ab initio* calculations for SF_6 at the 3-21G* level.

Comparison of gross orbital charges on sulfur and fluorine atoms indicates that bonding in the two conformers is similar. When compared with SF_6 results it appears that sulfur 3d orbitals play a slightly less important role in S_2F_{10} than in SF_6. This observation may be related to the large measured S–S bond length. Small differences between gross orbital charges on axial and equatorial fluorine atoms are likewise related to small but measurable bond length differences. Gross atomic charge on sulfur appears to be smaller in SF_6 than in S_2F_{10} thus indicating a possibly larger sulfur–fluorine electron transfer in the former compound.

TABLE 3. Mulliken population analysis and other properties

	S			F_a		F_e	
	s	p	d	s	p	s	p
Gross orbital populations							
$S_2F_{10}(D_{4d})$	5.047	8.277	0.803	3.990	5.365	3.996	5.383
$S_2F_{10}(D_{4h})$	5.043	8.289	0.804	3.990	5.366	3.996	5.381
$SF_6(O_h)$	4.909	8.051	0.842	3.989	5.378		
Gross atomic charges							
$S_2F_{10}(D_{4d})$		14.127		9.356		9.379	
$S_2F_{10}(D_{4h})$		14.134		9.356		9.378	
$SF_6(O_h)$		13.802		9.366			

	Electric quadrupole moment (10^{-40} Cm^2)		Dipole polarizability (10^{-40} C^{2}m^2 J^{-1})	
	$\theta_{xx} = \theta_{yy}$	θ_{zz}	$\alpha_{xx} = \alpha_{yy}$	α_{yz}
D_{4d}	−23.38	−22.94	4.94	6.34
D_{4h}	−23.36	−23.01	4.94	6.31

The energy level diagram in Fig. 1 emphasizes the similarity of the electronic structures of SF_6 and S_2F_{10}. The levels were derived from a photoelectron spectrum of SF_6 and good quality MO calculations [4]. Our *ab initio* results did not account for correlation energy so in order to make a comparison with SF_6, S_2F_{10} eigenvalues were scaled by the factor 0.92 towards lower binding energies ('92% rule', [5]).

With this somewhat arbitrary adjustment a comparison in Fig. 1 was made and showed that the 'two halves' of the S_2F_{10} molecule retained their identity to a considerable degree. This observation is similar to the results obtained for trifluoromethyl substituted compounds where due to strong fluorine electron affinity the CF_3 group's electronic structure remained almost intact [6].

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