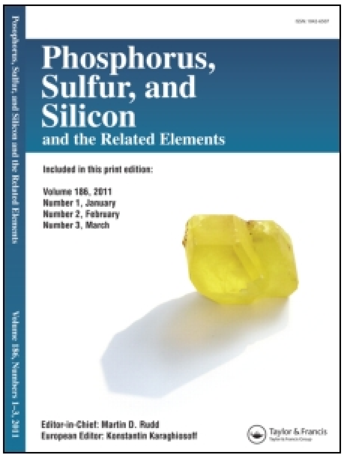

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LOWEST ENERGY DISTORTIONS IN HYPERVALENT SULFUR COMPOUNDS: THIAPENTALENES

David A. Dixon[a]; Anthony J. Arduengo III[a]
[a] Central Research and Development Department, E. I. du Pont de Nemours and Company, Wilmington, DE

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LOWEST ENERGY DISTORTIONS IN HYPERVALENT SULFUR COMPOUNDS: THIAPENTALENES

DAVID A. DIXON and ANTHONY J. ARDUENGO III
Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, DE 19880-0328
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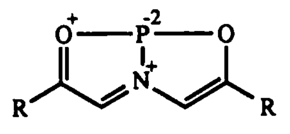
The molecular and electronic structures of two model thiapentalenes have been calculated with high quality *ab initio* molecular orbital theory. At the SCF level, the lowest energy structures correspond to in-plane distortions of a C_{2v} structure. The inclusion of a correlation energy correction leads to the symmetric C_{2v} structure having the lowest energy. The out-of-plane bending distortion has also been investigated and has shown to lead to much higher energy structures. These results are contrasted to the distortions calculated for ADPO which lead to a folded structure as the lowest energy structure at the SCF level. The different types of distortions are related to the charge and electronic nature of the central atom, S or P.

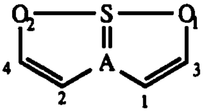
Key words: Thiapentalenes; hypervalent bond; edge inversion, molecular orbital theory.

The design of compounds containing main group elements in unusual bonding environments has had many successes in providing insight into novel types of molecular behavior.[1,2] The design of ADPO complexes led to structures with a

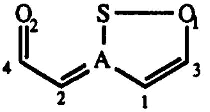


ADPO

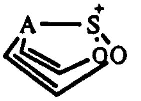
planar P with the ligands bonded in a T-shaped arrangement.[1] This led us to study the simple model systems, the fluorinated phosphines,[3] by molecular orbital theory and to the prediction of the edge inversion mechanism. This theoretical mechanism was verified experimentally in an ADPO analog.[4] Our calculations on ADPO and saturated and partially saturated derivatives have shown that the edge inversion process is the lowest energy mode in these structures.[2,4] This corresponds to folding of the molecule along the P-N axis. We have now calculated the structure of model thiapentalenes (**1a** + **2a**) which are isoelectronic to ADPO with A = C (giving a neutral) and A = N^+ (giving a cation). The lowest energy mode calculated for



1a A = C
2a A = N^+



1b A = C
2b A = N^+

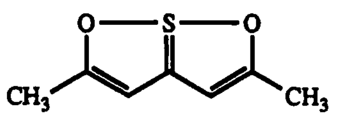


1c A = C^-
2c A = N

these structures corresponds to an in-plane bend as opposed to bending about the S-A bond. Here we contrast the in-plane and out-of-plane motions.

The calculations were done with the program GRADSCF[5] on CRAY 1A and X-MP computer systems. The geometries were optimized using gradient techniques[6] by minimizing the energy in the appropriate symmetry. Force fields were calculated at the optimum SCF geometries using the rapid analytic second derivatives[7] incorporated in GRADSCF. Correlation corrections were done at the SCF geometries at the MP-2 level[8] incorporating only the valence electrons. The basis set for sulfur is the split valence basis sets of McLean and Chandler[9] for the neutral, augmented by a set of d functions (a = 0.60). All of the atoms bonded to the sulfur have basis sets of double zeta quality augmented by a set of d polarization functions. The remaining atoms have double zeta basis sets.[10] The basis sets for these atoms (O, N, C, H) were taken from Dunning.[11]

In contrast to ADPO which shows a minimum for the C_{2v} structure at the SCF level, neither **1a** nor **2a** show such a minimum (See Table I). Both structures are transition states at the SCF level with one negative direction of curvature. The motion along the negative direction of curvature is an in-plane bend parallel to the 3c, 4e-hypervalent bond and corresponds to formation of the resonance structure **1b**. Such distortions are indeed well known in the asymmetrically substituted thiapentalenes.[12] At the SCF level, the C_{2v} structure (**1a**) is 3.9 kcal/mol above the C_s structure (**1b**).[13] The C_{2v} structure is lower in energy than the C_s structure by 7.4 kcal/mol at the MP-2 level for a total differential correlation effect of 11.3 kcal/mol. The X-ray crystal structure[14] for **3** (dimethyl substituted **1a**) shown below has C_{2v} symmetry in agreement with the correlated result. A similar result is found for



3

2 where the C_s structure (**2b**) is more stable than the C_{2v} structure (**2a**) at the SCF level by 6.6 kcal/mol but the C_{2v} structure (**2a**) is more stable at the MP-2 level by 14.5 kcal/mol. Here the effect of correlation is much larger, 20.1 kcal/mol.

TABLE I
Total (a.u.) and Relative (kcal/mol) Energies for 1 and 2

Molecule	E(SCF)	E(MP-2)
	Total	
1a(C_{2v})	−738.837848	−739.806933
2a(C_{2v})	−755.116302	−756.146236
	Relative	
1a(C_{2v})	0.0	0.0
1b(C_s)	−3.9	7.4
2a(C_{2v})	0.0	0.0
2b(C_s)	−6.6	14.5
2c(C_s)	25.8	53.0

The other alternative to an in-plane bend corresponding to distortion of the hypervalent bond is an out-of-plane bend about the S—A bond. This also leads to loss of the hypervalent bond and formation of a normally bonded trivalent S^+. In ADPO such a bend leads to a structure that is 9.9 kcal/mol more stable than the planar structure at the SCF level in contrast to the experimental result that shows that the structure is planar.[2] Inclusion of correlation leads to the planar structure being more stable by 13.8 kcal/mol, a correlation energy correction of 23.8 kcal/mol.[2] We also searched for such distorted structures in the two sulfur derivatives. The cation **2** has a bent minimum (**2c**). However, it is much higher in energy than in C_{2v} structure (**2a**) even at the SCF level. At the SCF level, it is 25.8 kcal/mol higher in energy and at the MP-2 level, the bent structure **2c** is 53.0 kcal/mol higher in energy. For the neutral sulfur derivative, there was no such minimum as the bent structure just relaxed back to the C_{2v} structure. These substantial energy differences suggest that a fully correlated treatment in the geometry optimization would not yield a second minimum on the potential energy surface.

The low-lying vibrational modes (Table II) are consistent with the energetic results. As stated above, the C_{2v} structures are transition states for going between the two valence bond structures and are characterized by one negative direction of curvature for **1** and **2**. In the in-plane C_s structure **1b**, the lowest lying frequency is the in-plane bend with the out-of-plane bends occurring at higher frequencies. For **2**, this situation is reversed and a high energy minimum is found for the out-of-plane C_s structure **2c**. For ADPO, the C_{2v} structure is a minimum and the lowest frequency is for an out-of-plane inversion process. The in-plane distortion frequency is much higher in energy and is of comparable magnitude to the value of the imaginary frequency calculated for **2a**. The two lowest lying frequencies for the out-of-plane structures for ADPO and **2a** are the same with a low value of 77 cm^{-1} for the inversion frequency.

We first compare our calculated structure for **1a** to the known experimental structure[14] of **3** (See Table III). The bond distances are calculated to be longer than the experimental distances by <0.03 Å except the calculated C—O bond distances are shorter than the experimental values.[15] These differences also show up in the bond angles as would be expected with differences between the calculated and experimental values of up to 4°. The structure of the C_s form (**1b**) shows a pronounced shortening of one S—O bond and a lengthening of the other S—O bond. In fact, the latter distance is so long that only a weak interaction exists between this O and the S. However, there still is some interaction between the

TABLE II
Low-Lying Vibrational Frequencies (cm^{-1})

Molecule	In-plane	Out-of-plane	Out-of-plane
1a(C_{2v})	299i	230	239
1b(C_s)	154	183	202
2a(C_{2v})	394i	238	249
2b(C_s)	187	156	196
2c(C_s)	241	79	
ADPO(C_{2v})	373	140	
ADPO(C_s) folded	231	76	

TABLE III

Geometries for 1 and 2 C_s and C_{2v} Conformers[a]

Prop	**1b**(C_s)	**1a**(C_{2v})	3(C_{2v}) expt	**2b**(C_s)	**2a**(C_{2v})	**2c**(C_s)
			Bond Distances			
S—O_1	1.696	1.889	1.865	1.659	1.815	1.572
S—O_2	2.463	1.889	1.865	2.414	1.815	1.572
S—A	1.748	1.733	1.702	1.750	1.725	1.702
A—C_1	1.447	1.404	1.381	1.418	1.345	1.452
A—C_2	1.359	1.404	1.381	1.284	1.345	1.452
O_1—C_3	1.335	1.278	1.305	1.334	1.266	1.425
O_2—C_4	1.221	1.278	1.305	1.201	1.266	1.425
C_1—C_3	1.346	1.382	1.356	1.338	1.393	1.319
C_2—C_4	1.443	1.382	1.356*	1.482	1.393	1.319
C_1—H_1	1.066	1.066		1.064	1.064	1.066
C_2—H_2	1.069	1.066		1.070	1.064	1.066
C_3—H_3	1.070	1.074		1.067	1.071	1.064
C_4—H_4	1.085	1.074		1.078	1.071	1.064
			Bond Angles			
O_1—S—A	92.0	85.8	87.0	90.4	84.1	95.8
O_2—S—A	77.3	85.8	87.0	76.0	84.1	95.8
O_1—S—O_2	169.4	171.7	173.9	166.4	168.3	110.2
S—A—C_1	108.2	114.8	113.9	109.7	116.8	106.4
S—A—C_2	123.0	114.8	113.9	124.8	116.8	106.4
S—O_1—C_3	111.8	111.4	115.0	113.6	114.9	112.1
S—O_2—C_4	101.9	111.4	115.0	105.0	114.9	112.1
C_1—A—C_2	128.9	130.4	132.2	125.5	126.4	113.6
A—C_1—C_3	111.4	110.9	113.4	110.7	110.2	113.0
A—C_2—C_4	116.8	110.9	113.4	117.1	110.2	113.0
O_1—C_3—C_1	116.7	117.0	115.0	115.6	114.0	112.4
O_2—C_2—C_4	121.0	117.0	115.0	117.1	114.0	112.4
A—C_1—H_1	123.5	123.9	118.7	120.6	121.7	119.0
C_3—C_1—H_1	125.1	125.3	127.9	128.7	128.1	128.0
A—C_2—H_2	121.9	123.9	118.7	120.2	121.7	119.0
C_4—C_2—H_2	121.3	125.3	127.9	122.6	128.1	128.0
O_1—C_3—H_3	115.4	118.2	116.2	116.6	120.3	114.4
C_1—C_3—H_3	127.9	124.7	128.8	127.8	125.8	133.1
O_3—C_4—H_4	120.2	118.2	116.2	123.7	120.3	114.4
C_2—C_4—H_4	118.8	124.7	128.8	119.2	125.8	133.1

[a]Bond distances in Å. Bond angles in degrees.

more distant oxygen and the sulfur which constrains the system to remain planar and for the bonds in the backbone to remain partially delocalized. The S—C bond length changes only slightly on distortion. The bond distances from the C bonded to the S(C_A) to the carbons change following the above valence bond structure. The C_A—C_1 bond increases and the C_A—C_2 bond decreases. The O_1—C_3 bond length in the ring increases whereas the O_2—C_4 bond length decreases to almost the value of a carbonyl group. The C_1—C_3 bond length in the ring decreases towards the value expected for a C=C whereas the C_2—C_4 bond has significantly more C—C single bond character. The bond angles show the expected changes based on the changes in the bond lengths.

Substitution of N^+ for C to generate the cation **2a** leads to the expected changes in the C_{2v} structure. The S—O bonds shorten by 0.07 Å, but the S—N bond is only 0.01 Å shorter than the S—C bond in **1a**. The C—N bonds shorten as expected. The C—C bonds lengthen and the C—O bonds shorten. The changes in the angles are consistent with the changes in the bond lengths. The in-plane C_s distorted structure **2b** follows the distortions found in **1b** to give the expected valence bond structure. The S—O_2 interaction is somewhat shorter in **2b** as compared to **1b** consistent with the larger positive charge on the S in the former. The C=O carbonyl bond is shorter in **2b** as is the N_A=C_2 bond as compared to the C_A=C_2 bond. The C_2—C_4 single bond is even longer in **2b** than in **1b**. The out-of-plane C_s structure **2c** also shows significant changes in geometry. The hypervalent bond at S is lost and the S—O bond distances get much shorter, 0.24 Å. The S—N distance only shortens by 0.02 Å. Since the rings do not delocalize, the C—C bond distances become more double bond like and the C—O and C—N distances more single bond like. These changes are all substantial with the C—C bonds shortening by 0.07 Å and the C—N and C—O bonds lengthening by 0.11 and 0.16 Å, respectively. With the large changes in bond lengths and electronic structure, the bond angles also show large changes. The bonding at S becomes pyramidal with bond angles of 96° and 110° as does the bonding at N with bond angles of 113° and 114°. The remaining ring bond angles adjust to accommodate these with the constraint of a C=C double bond in a five-member ring.

The Mulliken charges are given in Table IV. The positive charge on the S increases from the C_s in-plane structure **2b** to the C_{2v} structure **2a** to the C_s out-of-plane structure **2c**. The positive charge is highly localized on the S and is greater than +1 in **2c**. The negative charges on O are weakly dependent on geometry. The largest change is in the charge on N which becomes more negative by 0.26 e in **2c** as compared to **2a**. This accounts for most of the excess positive charge on the S. In **2b**, the charges are no longer equal in each "ring" but the pattern of charges is the same. For **1**, similar patterns are predicted. The nominally positively charged S has only about one-half of the positive charge associated with the simple valence bond structure. The most surprising result is that the C_A bonded to S is also positive when simple valence bond arguments would make it negative. The C atoms bonded to the C_A are quite negative and the other two C atoms (bonded to O) are quite positive. The O atoms are negatively charged as expected but the negative charge on the O is only increased by 0.08 e as compared to **2** even though **1** is formally neutral.

Although the electronic structures of **1** and **2** appear to be quite similar to that

TABLE IV
Mulliken Charges (e) for 1 and 2

Atom	**1b**(C_s)	**1a**(C_{2v})	**2b**(C_s)	**2a**(C_{2v})	**2c**(C_s)
S	0.49	0.58	0.80	0.92	1.30
O_1	−0.59	−0.63	−0.54	−0.55	−0.55
O_2	−0.56	−0.63	−0.44	−0.55	−0.55
A	0.21	0.23	−0.35	−0.32	−0.58
C_1	−0.35(−0.12)	−0.44(−0.19)	−0.05(0.24)	−0.07(0.23)	0.00(0.30)
C_2	−0.45(−0.22)	−0.44(−0.19)	0.04(0.33)	−0.07(0.23)	0.00(0.30)
C_3	0.12(0.37)	0.20(0.42)	0.17(0.47)	0.23(0.52)	0.09(0.39)
C_4	0.23(0.40)	0.20(0.42)	0.24(0.49)	0.23(0.52)	0.09(0.39)

of ADPO, there are clear differences in the way the molecules distort. These low energy distortions provide a probe of the nature of the electronic structure. The sulfur has more electron density as compared to the phosphorus. Because sulfur can support two lone pairs when it is in its 8-S-2[16] arrangement (normal Lewis structure), **1** and **2** undergo an in-plane distortion which yields the 8-S-2 arrangement and minimizes repulsions in the electron-rich sigma system. The more electropositive phosphorus usually only possesses a single lone pair of electrons in its 8-P-3 arrangement (normal Lewis structure) and the minimum energy distortion of ADPO is an out-of-plane folding that tends to the 8-P-3 arrangement.

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