Computational design of Oligo-sulfuranes

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Abstract. We studied the effect of electronegativity perturbation on the isolobal behavior of tetra-coordinate hypervalent compounds of S (sulfuranes, SL_4 , L is any atom or group which can provide one electron for S-L bonding). Though formally the fragment SL_4 obtained from SL_6 is an isolobal equivalent of CH_2 , a qualitative molecular orbital study shows that only SF_2H_2 with equatorial F atoms is a practical isolobal substitute for CH_2 and can form oligomers, $(SF_2H_2)_2$, (**14**), $(SF_2H_2)_3$, (**15**) and $(SF_2H_2)_4$, (**16**) analogous to ethylene, cyclopropane and cyclobutane, respectively. DFT computations at the B2PLYP/6-311++g(d,p), MP2/aug-cc-pVTZ and B3LYP/6-311++g(d,p) levels confirm these structures to be minima on the PES. The skeletal S-S bonds in these structures are formed solely by the bonding combination of anti-bonding fragment orbitals of SF_2H_2 . In contrast, per-fluorination, the usual way to stabilize hypervalent structures, is found to have an opposite effect here. Calculations at the same levels show $(SF_4)_2$, $(SF_4)_3$, and $(SF_4)_4$ not to be minima. The highly stable HOMO of SF_4 fragment and large HOMO-LUMO gap makes SF_4 a stable entity, preventing it from oligomerization. Out of the various isomers of SF_nH_{4-n} , $n = 0-4$, only SF_2H_2 with equatorial F atoms can form oligomeric sulfuranes. Substitution of F by heavier analogs of the group did not lead to any stable oligomers.

Keywords. Sulfuranes; isolobal analogy; oligo-sulfuranes; electronegativity perturbation.

1. Introduction

After a century of Lewis 2c-2e bond, hypervalent molecules that defy the rule still draw attention.¹ This is especially so for cyclic molecules with hypervalent atoms.² We present here an electronic structure study of a family of possible cyclic sulfuranes. Sulfuranes are well known synthetic reagents.³⁻¹⁰ The Martin sulfuranes, for example, are used for a variety of reactions like dehydration, amide cleavage, epoxide formation, *etc.*³⁻¹⁰ Sulfuranes with the exception of SH_4 ,¹¹ have butterfly-like structure, which can be visualized as a trigonal bipyramid (TBP), with an equatorial vertex replaced by a lone pair (Figure 1).^{12,13} An analysis of the bonding in sulfuranes (SL_4 , L = any atom or group which can provide one electron for S-L bonding) has shown that electronegative substituents prefer to occupy the axial position, a behavior similar to that of TBP-phosphorus.^{12,13} Thus, SL_4 can be considered, both in terms of its geometry and substituent preferences, as originated from a TBP structure. An isolobal analysis of sulfuranes¹⁴ reveals some new aspects (Figure 2). If

SL_4 is considered to be originated from TBP SL_5^+ , SL_4 is isolobal to CH_3^- , which in turn implies that PL_4 and the isoelectronic SiL_4^- are isolobal to CH_3 radical (Of course, this is not the right way to generate isolobal fragments, as we also need to worry about the symmetry and energy of the frontier orbitals; we will be taking care of those aspects later). Many compounds are known where SiL_4^- dimerizes like CH_3 radical.¹⁵⁻¹⁹ We looked at SL_4 in a different perspective. If we consider SL_4 as a fragment derived from SL_6 (Figure 2), can it be isolobal to CH_2 ? If so, can it form dimer, trimer *etc.*, as CH_2 does (Figure 3)? Our attempt to answer this question led to the prediction of a new class of compounds, oligo-sulfuranes. The study also revealed a strong dependence of the isolobal behavior of hypervalent fragments on the nature and position of substituents.

2. Computational Details

Computations at the B2PLYP/6-311++g(d,p) level were used to verify our predictions based on qualitative molecular orbital theory.^{20,21} The double hybrid density functional B2PLYP is an improvement over B3LYP by including perturbative second order correlation.²¹

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Figure 1. Formation of sulfurane (SL_4) from trigonal bipyramidal SL_5^+ .

Frequency analysis is done on the optimized geometries to locate minima on the potential energy surface. Computations were done also at the B3LYP/6-311++g(d,p) level and MP2/aug-cc-pVTZ level as well and the results are similar.^{22–25} For discussion, we use the results obtained from B2PLYP/6-311++g(d,p) level of computations. Coordinates and energies of the structures discussed are given in the Supporting Information.

3. Results and Discussion

Optimization of structures **2** and **3** with $L = H$, resulted in collapse to the sulfurane fragments. This prompted us to try $L = F$, as it is already known that F atoms can stabilize hypervalent structures and we have proposed an unusual system stabilized by F atoms, $(PF_3)_3^{2-}$.² To our surprise, even perfluorination could not stabilize structures **2** and **3**. This implies that we need to look into the details of frontier orbitals of sulfurane fragments and their isolobal relationships.

The frontier orbitals of SH_4 (**4**) (Figure 4, b) shows that they have the same symmetry as the frontier

Figure 2. Formation of tetra-coordinate hypervalent fragment and their isolobal relationships to the fragments of CH_4 .

Figure 3. Formation of the oligomers of sulfuranes; L is any atom or group which can provide one electron for S-L bonding.

orbitals of CH_2 (Figure 4, a), but energetically, the former must be higher in energy as they are anti-bonding orbitals (Refer Table 1 for the coefficients and energy values). The SH_4 fragment is created by the removal of two H atoms from SH_6 and CH_2 fragment is created by the removal of two H atoms from CH_4 . This was done so, as the butterfly structure of SH_4 cannot be obtained as a stationary point. The calculations are for singlet. The frontier orbitals of CH_2 are localized over C atom, whereas in SH_4 they are delocalized over S and H atoms. Thus, the interaction between the S atoms of two SH_4 fragments will not be as stabilizing as the interaction between the C atoms of two CH_2 fragments.

It is reasonable to assume that for any sulfurane to imitate CH_2 , there must be significant coefficient of the frontier orbitals on the S atom. The frontier orbital coefficient on S in sulfurane depends on the energy difference between the S atom orbitals and the Symmetry Adapted Linear Combination (SALC) which interact with it. This is represented schematically in Figure 5; the three situations, (1) the energy of SALC is very high

Figure 4. (a) Frontier orbitals of CH_2 (singlet); (b) Frontier orbitals of SH_4 ; (c) Symmetry Adapted Linear Combinations (SALCs) corresponding to the frontier orbitals of SH_4 .

Table 1. Percentage contributions from the atomic orbitals to the frontier orbitals of **4–7** and their energy values in eV. Comparison to singlet CH₂ is also shown.

°	HOMO coefficient on S		LUMO coefficient on S	HOMO Energy/eV	LUMO energy/eV
°	s(S)	p(S)			
4	0	15	19	–5.5	0.5
5	0	40	91	–8.4	–2.6
6	20	32	15	–10.2	0.1
7	23	20	92	–11.9	–2.5
CH₂				–8.3	–1.8

compared to the p orbitals of S atom (**a** & **d**); (2) the energy of SALC is comparable to the p orbitals of S atom (**b** & **e**); (3) the energy of SALC is lower than the p orbital of S atom (**c** & **f**), are shown. The large size of the orbitals in Figure 5 indicates large coefficients. The antibonding combinations in **a**, **b** and **c**, respectively, form the HOMO of the sulfurane when the energy of the SALC is >, = or < the energy of the p orbital in S. The diagrams are constructed based on the simple logic

that the bonding MOs will have large coefficients from the lower energy fragment orbitals and the antibonding MOs will have large coefficients from the higher energy fragment orbital (the fragments in the sulfurane, SL₄ are S and L₄). To remind, a better comparison to the HOMO of singlet CH₂ will be when the coefficient on S is large. Comparing the antibonding MOs in **a**, **b** and **c**, one can immediately avoid **a**, as the coefficient over S is less. The antibonding MO in case **c** has significant

Figure 5. a, b and c- interaction of the SALC of sulfurane with the orbitals on S to form the bonding and antibonding combinations, where the antibonding one forms the HOMO of sulfurane. Diagrams a, b and c correspond to situations when the SALC energy is >, = or < the energy of the p orbital of S; d, e and f- interaction of the SALC with the p orbital on S to form the bonding and antibonding combinations, where the antibonding one forms the LUMO of sulfurane. Diagrams d, e and f correspond to situations when the SALC energy is >, = or < the energy of the p orbital of S.

Figure 6. The highest energy SALCs of sulfurane: Substitution of F atoms in the equatorial position slightly stabilizes SALC1 and significantly stabilizes SALC2.

coefficient over S, but the large mixing of the s orbital will tend to make it inert. Thus, the antibonding MO in **b** remains as a reasonable comparison to the HOMO of CH_2 (singlet). The antibonding combinations in **d**, **e** and **f**, respectively, form the LUMO of the sulfurane when the energy of the SALC is $>$, $=$ or $<$ the energy of p orbital in S. Comparing **d**, **e** and **f**, the antibonding combination in **f** seems to be the best comparison to the LUMO of CH_2 (singlet) as the coefficient over S is maximum. The only thing we need to do now is to create the sulfurane in such a way that its HOMO resembles the antibonding combination in **b** and its LUMO resembles the antibonding combination in **f**. That means a moderate stabilization of SALC1 and huge stabilization of SALC2 (Figure 6). How can this be achieved? If the high coefficient sites of SALC1 are occupied by F, it is highly stabilized. If the low-coefficient sites are

occupied by F, it is moderately stabilized. Now, the SALC2 can be stabilized significantly by substituting F atoms in the equatorial position. Thus, SF_2H_2 with equatorial F atoms will be the best comparison to CH_2 .

The sulfuranes we considered are shown in Figure 7, so chosen, as to match the symmetry of CH_2 and also to invoke electronegativity perturbation. Our qualitative arguments are difficult to support by quantitative diagrams or numbers because of several reasons: (1) Since there are lone pairs on F, which often mix with the radial orbital combinations, it is difficult to show a one-to-one relationship between the qualitative MO pictures and the computed MOs; (2) The sulfurane geometries considered are not the optimized geometries, they are constructed by the removal of adjacent H atoms from the corresponding persulfuranes, as indicated in Figure 7 (these persulfuranes were studied computationally by Steudel *et al.*²⁶). This was necessary, as the structures **4** and **5** cannot be obtained as stationary points after optimization. Nevertheless, we report here the computed frontier orbital coefficients and energy values of the sulfuranes **4–7** (Table 1). The correlation with the qualitative arguments is evident. The frontier orbital energy values of CH_2 (singlet) and **5** are comparable. Thus, **5** seems to be the best isolobal substitute for CH_2 . Triplet state of **5** is a minimum and the energy values of the singly occupied orbitals are very close to those of triplet CH_2 (-9.5 eV, -8.5 eV for CH_2 and -9.6 eV, -8.3 eV for SF_2H_2). On the other hand, the singlet state of **5** is not a stationary point; it converges to **6** during optimization. It was already shown computationally that the most stable structure of SF_2H_2 is **6**.^{27,28} The large s character of the HOMO and the large HOMO-LUMO gap makes **6** and **7** stable molecules as such (Table 1). The computed frontier orbitals of all the sulfurane fragments considered, are shown in Figure 8, along with the frontier

Figure 7. SH_4 and $\text{SF}_n\text{H}_{4-n}$ with C_{2v} symmetry. They are constructed by the removal of adjacent H atoms (shown in dotted ellipse) from the corresponding persulfuranes. Comparison to CH_2 formation from CH_4 is also shown.

Figure 8. Comparison of the frontier orbitals of sulfuranes **4–7** computed, to those constructed by qualitative MO theory.

orbitals constructed based on the analysis shown in Figure 5. The actual picture looks slightly different in the case of the HOMOs of **6** and **7**. The HOMOs of **6** and **7** can be better described by an interaction as shown in Figure 9.

In agreement with the previous analysis, the sulfuranes, **4**, **6**, **7** and SF_2H_2 with one equatorial and one axial F, which are not good isolobal analogs of CH_2 could not form structures similar to **2** and **3**. On the other hand, structure **5**, which is shown to be a better isolobal analog of CH_2 , gave dimeric and oligomeric structures as minima, analogous to ethylene and cycloalkanes (Figure 10). Oligomeric structures with F atoms replaced by other halogens are not minima, as with other halogens the antibonding coefficient on S decreases (the electronegativity perturbation will be less with other halogens). The S-S bond length in the dimeric structure, $(\text{SF}_2\text{H}_2)_2$ (**14**) is 1.955 Å, which is close to the S-S bond length of S_2 (1.926 Å) calculated at the same level. The HOMO-LUMO gap is 8.5 eV. The trimeric sulfurane, $(\text{SF}_2\text{H}_2)_3$ (**15**) analogous to cyclopropane, is a minimum with a HOMO-LUMO gap of 8.2 eV; the S-S bond length is 2.222 Å. The tetrameric sulfurane, $(\text{SF}_2\text{H}_2)_4$ (**16**) is also found to be a minimum with a HOMO-LUMO gap of 7.7 eV and an S-S bond length of 2.271 Å. Its puckered structure is similar to that of cyclobutane.

Figure 9. Interaction of the SL_2 fragment with L_2 to generate SL_4 ; only the interaction of the radial orbital of SL_2 is shown; The antibonding combination is similar to the HOMO of **6** and **7** obtained by computations.

The binding energy of the structures **14–16** with respect to the triplet SF_2H_2 fragments ($E((\text{SF}_2\text{H}_2)_n) - nE(\text{SF}_2\text{H}_2)$) are -53.2 kcal/mol, -72.6 kcal/mol and -101.0 kcal/mol, respectively, at 298.15 K. These large negative values indicate thermodynamic stability with respect to the dissociation into SF_2H_2 fragments. Thus, the fragmentation of oligo-sulfuranes to SF_2H_2 fragments will be difficult. But other lower energy fragmentation paths are possible which generates multiple fragments and involves elimination of H_2 or HF (the transition states and the Intrinsic Reaction Coordinate (IRC) plots are given in the Supporting Information). The barrier for dissociation through these lower energy pathways for di-, tri- and tetramers of SF_2H_2 are 5.2 kcal/mol, 10.2 kcal/mol and 9.9 kcal/mol, respectively, which are very small, thereby making the experimental realization of these molecules very difficult. In spite of that, these barriers are enough for their fleeting existence in low temperature matrices.²⁹ Structures **14–16** are model systems which show the utility of qualitative MO theory to predict new bonding patterns. An experimental realization would require severe stabilizing methods. Higher homologues like $(\text{SF}_2\text{H}_2)_5$, $(\text{SF}_2\text{H}_2)_6$, etc., are also minima (See Supporting Information for the coordinates of $(\text{SF}_2\text{H}_2)_5$ and $(\text{SF}_2\text{H}_2)_6$), though the proximity of the atoms would make them highly unstable.

Figure 10. $(\text{SF}_2\text{H}_2)_n$ ($n = 2, 3, 4$) and the S-S bonding MOs; blue spheres are F and pink spheres are H.

The entry of anionic oligomers of CO and PF_3 in literature showed us examples for skeletal bonding involving fragment antibonding orbitals.^{2,30} In these molecules, one fragment orbital is the radial non-bonding orbital and the other is antibonding orbital. The unusual feature of structures **14–16**, is that both of their fragment frontier orbitals are antibonding; no surprise that they are less stable kinetically. Thus, these molecules form a unique class of compounds, where the oligomeric skeleton is formed solely by the monomeric σ^* and pseudo- π^* orbitals. Similar bonding is noted in the pancake-type π -stacking interactions, where π^* orbitals of two molecules interact.³¹

The isolobal analogy in the transition metal fragments depends less on the substituents on the transition metal. The ML_4 fragment (M is a transition metal) generated from ML_6 , can be equated to CH_2 fragment if the frontier orbital of ML_4 has 2 electrons. On the other hand, the SH_4 fragment generated from SH_6 is not isolobal to CH_2 . Out of the various isomers of $\text{SF}_n\text{H}_{4-n}$ ($n = 0-4$), SF_2H_2 (**5**) is the only structure that can form oligomers as CH_2 does. Thus the isolobal behavior of hypervalent fragments depends strongly on the nature and position of the substituents.

4. Conclusions

We have analyzed the isolobal behavior of sulfurane fragments based on qualitative molecular orbital theory

and electronegativity perturbation. We show that SF_2H_2 with equatorial F atoms is a good isolobal substitute for CH_2 . Thus, the oligo-sulfuranes, $(\text{SF}_2\text{H}_2)_2$, $(\text{SF}_2\text{H}_2)_3$ and $(\text{SF}_2\text{H}_2)_4$, are minima, and form the hypervalent analogs of ethylene, cyclopropane and cyclobutane. The skeletal S-S bonding orbitals in these structures are formed from the SF_2H_2 -antibonding orbitals. Since the large electronegativity perturbation induced by F atoms is responsible for their stability, structures with other halogen atoms are not minima. Contrary to typical hypervalent structures which are stabilized by per-fluorination, oligo-sulfuranes decompose on per-fluorination; $(\text{SF}_4)_2$, $(\text{SF}_4)_3$ and $(\text{SF}_4)_4$ are not minima. Thus, we show that it is possible to stabilize hypervalent structures, which are quite unstable otherwise, by properly adjusting the positions of electronegative atoms, so as to create orbitals of proper symmetry.

Supplementary Information (SI)

Coordinates of the structures are given in the Supporting Information, available at www.ias.ac.in/chemsci.

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