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FEATURE ARTICLE

# Hypervalent molecules, sulfuranes, and persulfuranes: review and studies related to the recent synthesis of the first persulfurane with all substituents carbon-linked

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**Abstract** In his classic 1969 review, Jeremy Musher introduced the term “hypervalent” to describe molecules composed of main group elements failing to satisfy the octet rule. Since that time, there has been much progress in the preparation and understanding of hypervalent molecules. Theoretical research from our group on sulfuranes and persulfuranes, two of the most important classes of hypervalent molecules, is reviewed in the first part of this Account. The immediate motivation for the new research reported here was the recent synthesis of the novel hypervalent persulfurane with all carbon ligands, *cis*-bis(2,2′-biphenylylene)dimethylpersulfurane $(C_{12}H_8)_2(CH_3)_2S$, (Sato et al. J Am Chem Soc 128:6778, 2006), representing a landmark advance in main group chemistry. We have theoretically studied the synthesized compound, as well as its two *trans* forms, using density functional methods. Our theoretically optimized geometry for the *cis* structure is in good agreement with the experimental structure. Sulfur *d* orbital participation is relatively unimportant in the bonding. The *trans*-1 and *trans*-2 structures, which have not been observed experimentally, are predicted to be genuine minima, lying in energy above the *cis* structure by ~16 kcal/mol due to the strain of the geometric distortions. Two transition states for the relevant isomerizations have been located, and the energy barriers are discussed.

**Keywords** Hypervalent molecules · Sulfurane · Persulfurane · DFT

## 1 Hypervalent molecules

We typically think of hypervalent compounds as rather exotic and not very stable [1, 2]. However, the well-known example of $SF_6$ cautions us in this regard. Sulfur hexafluoride was discovered in 1901 by Moissan and Lebeau [3], the former receiving the Nobel Prize in chemistry 5 years later for his research in fluorine chemistry. As is well known for environmental reasons, $SF_6$ is a uniquely stable molecule by any criterion. $SF_6$ was, however, not the first hypervalent sulfur compound to be made. That honor goes to $SCl_4$, reported in 1873 by Michaelis and Schifferdecker [4, 5] from the reaction of $S_2Cl_2$ with gaseous chlorine.

The term “hypervalent” became widely accepted in the chemistry community following the well-known review of Jeremy Musher [6] in *Angewandte Chemie*. Musher was a gifted theoretical chemist who died tragically of a brain tumor before reaching the age of 40. Those of us who knew Jeremy personally recall him as an extraordinarily challenging and charming human being. Musher is remembered by the Jeremy Musher Memorial Lecture at the Hebrew University. Musher defined hypervalent molecules as those “formed by elements in groups V–VIII of the periodic table in any of the valences other than their lowest stable chemical valences of 3, 2, 1, and 0, respectively.” In 1984

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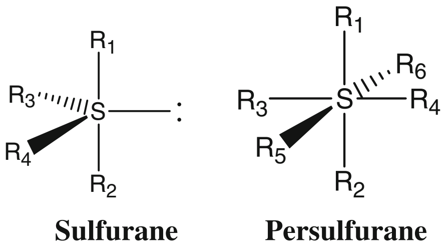


**Scheme 1** Sulfuranes and persulfuranes

Schleyer [7] suggested the term “hypercoordinated” chemistry to include an even broader class of compounds. Many others [1, 2, 8–16] have made important contributions to the understanding of bonding in hypervalent molecules.

$SF_6$ belongs to the category of persulfuranes (Scheme 1), which have 12 formal electrons around the sulfur atom.

It is known that highly electronegative substitutents (ligands) stabilize such hypervalent compounds, which possess 3c–4e bonds [17, 18]. Outstanding examples are the classes of sulfuranes and persulfuranes with halogen ligands. As noted above, $SF_6$ is the best known persulfurane, and its extraordinary stability is attested by current environmental concerns, while its hybrid counterpart $SH_6$ has not been prepared to date. The chlorosulfuranes (with less electronegative ligands) have also been synthesized, although they are usually less stable than their fluoro counterparts. In 1971 the first stable oxysulfurane (diaryldialkoxysulfurane) was prepared by the group of J. C. Martin. A series of important papers concerning the tetracoordinate sulfur compounds with oxygen-centered ligands were subsequently published by the same research group (The first three papers in the series are given in Refs. [19–21]). This family of isolable oxysulfuranes was reviewed by Martin in 1976 [22].

## 2 Brief theoretical review of hypervalent molecules

Our research group has been fascinated by hypervalent molecules for some time. The earliest (1972) work, with Bagus and Liu, involved the $KrF_2$ molecule. This and subsequent (1975) research [23, 24] on $XeF_2$ established the validity of Coulson’s 1964 model [25] for the bonding in these noble gas molecules. A final (1995) investigation in this area, with Crawford [26], highlights the deficiencies of the nonrelativistic Hartree–Fock method for the theoretically treacherous $XeF_6$ system.

The earliest ab initio study of the parent sulfurane ($SH_4$) and persulfurane ($SH_6$) was reported [8] with Schwenzer in 1975. This was followed the same year by research with Radom [27] on the $SF_4$ molecule, for which comparison with the experimental microwave structure of Tolles and Gwinn [28] was possible. The purported observation of the sulfurane $SF_2H_2$ by two experimental groups [29, 30] caused Ignatyev and one of us to examine this molecule theoretically. Unfortunately, it was concluded that the experimental infrared spectra had been misassigned. Our other two articles [31, 32] on the parent sulfurane $SH_4$ involved the barrier [33] for dissociation to $H_2S + H_2$. The final predicted zero-point corrected enthalpy ($\Delta H_0^{\ddagger}$) of the $C_1$ transition state is 16 kcal/mol above the $C_{4v}$ equilibrium geometry. This result and the predicted vibrational frequencies and IR intensities give hope for the future observation of $SH_4$.

The 1996 study with King and Galbraith [34] was directed toward the radical anions of the hypervalent species $SF_4$, $SF_5$, and $SF_6$. This in turn led to a theory–experiment collaboration with Marilyn Jacox [35] for the identification of several $SF_n$ cations and anions. Research with Brinkmann [36] dealt with theoretical challenges associated with the prediction of the electron affinity of $SF_6$. We have reported analogous investigations [37–42] of the neutral molecules and anions of $SiF_5$, $GeF_5$, $AsF_6$, $ClF_n$ ($n = 2, 4$), $BrF_n$ ($n = 2$–$7$), and $BrClF_n$ ($n = 1$–$4$). The last of the two above studies led to an investigation [43] of the hypervalent dibromine fluorides $Br_2F_n$ ($n = 1$–$6$). The “avoidance” of hypervalency was addressed for simple substituted $BrF_3$ and $BrF_5$ structures [44]. Specifically, it was discovered that the hydrogen bonded complex $BrF \cdots HF$ lies below the expected trivalent $BrF_2H$ analogous to $BF_3$. Similarly, the degree of hypervalency displayed by $BrF_5$ is reduced for $BrF_4H$, for which the hydrogen bonded complex $BrF_3 \cdots HF$ lies lower in energy. The same pattern is anticipated for $PF_4H$, $SF_3H$, $SF_5H$, $ClF_2H$, $ClF_4H$, $AsF_4H$, $SeF_3H$, and $SeF_5H$.

Even more complicated electronically than the fluorides are the hypervalent main group oxides. This research began (with Tim van Huis [45]) by challenging pyramidal $C_{3v}$ symmetry structure of $ClO_4$ deduced from infrared experiments [46]. We were able to show conclusively that the true $C_{2v}$ equilibrium geometry of $ClO_4$ yields the observed fundamentals in a much more satisfactory manner. Subsequent research [47, 48] involved the $ClO_2$ and $ClO_3$ molecules. Although not well characterized in the laboratory, the hypervalent bromine oxides $BrO_n$ ($n = 1$–$4$) and $Br_2O_n$ ($n = 1$–$4$) are potentially important for atmospheric chemistry and have therefore been subjected to theoretical investigation [49, 50]. Finally, we have studied [51] the novel bromine oxyfluorides $BrOF_n$ ($n = 1$–$5$).

The conjunction of aromaticity and hypervalency has been considered with Joe Thrasher for the $C_5H_5SF_3$ molecule [52]. The results were explained in terms of directional repulsion effects of $\pi$ bonds, apicophilicity of substituent groups in trigonal bipyramidal systems, and Bent's rule. A related study [53] of $SF_5CF_3$ and its anion reported integrated infrared intensities and discussed the implications for global temperature patterns.

The first synthesis of a peralkylated derivative of a hexavalent main group element was reported by Ahmed and Morrison [54] in 1990. Their pioneering synthesis of $Te(CH_3)_6$ led to Fowler and Hamilton's theoretical study [13] of the three isovalent molecules $S(CH_3)_6$, $Se(CH_3)_6$, and $Te(CH_3)_6$. The predicted structures are of $D_3$ symmetry, but only slightly distorted from octahedral ligand coordination. A second article with Ken Raymond [14] examined the same three molecules in the rare (for molecules) $S_6$ point group. The $S_6$ structures lie 0.3–0.7 kcal/mol higher than the analogous $D_3$ structures, and the energy differences are explained in terms of steric considerations, which are most important for the sulfur hexamethyl.

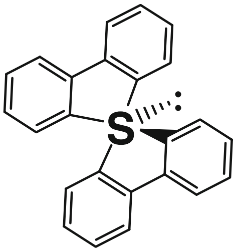
In a series of articles [55–58] with Schreiner, Schleyer, Schuurman, Allen, Speakman, and Turney, the potentially hypervalent $BH_5$, $AlH_5$, and $GaH_5$ molecules have been considered. The $BH_5$ system has been considered with truly state-of-the-art theoretical methods, yielding a dissociation ($BH_5 \rightarrow BH_3 + H_2$) energy $D_e = 6.6$ kcal/mol. Earlier matrix isolation IR assignments [59] for the $\nu_2$ and $\nu_9$ stretching modes of $BH_5$ compare favorably with theory [56], but the laboratory $\nu_6$ bending mode of the $BH_3$ subunit is not supported by the theoretical isotope shifts. The existence or nonexistence of $GaH_5$ has been widely discussed [60]. However, we predict $GaH_5$ to be bound by only $D_e = 2.1$ kcal/mol. Nevertheless, the agreement with a tentative experimental assignment [61] of the H–H stretching fundamental is satisfactory.

We conclude this brief theoretical review by noting two areas of research with Igor Ignatyev [62, 63]. The first is a study of the role of hexacoordinated silicon intermediates in the hydrolysis and racemization reactions of silyl halides. The examination of these $SiH_3F(H_2O)_2$ and $SiH_3Cl(H_2O)_2$ intermediates was continued to include the family $SiX_4Y_2$ (X = H, F, Cl), where Y is either water or ammonia.

With the brief review in mind, we turn to the research now being reported for the first time in our hypervalent molecule odyssey. The research that follows relates directly to the most important experimental advance of the past decade in sulfurane chemistry.

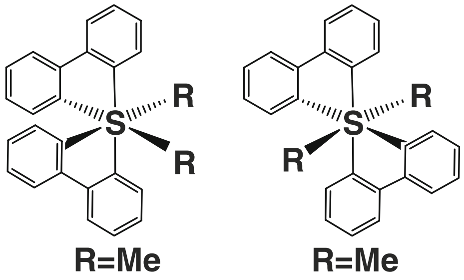
## 3 Immediate motivation

The sulfuranes and persulfuranes with all carbon ligands (i.e., the hypervalent organosulfur compounds) are difficult to prepare. For example, $Me_4S$ was predicted by theory in 1994 to be a minimum on its potential energy hypersurface [64]; however, it has not been prepared experimentally, probably due to the fact that it is thermodynamically unstable with respect to $Me_2S$ and ethane [65]. To stabilize sulfuranes with all carbon ligands, $R_4S$, one effective way (thermodynamic stabilization) is to increase the electronegativity of R, for example, using $R = C_6F_5$ [66]. This strategy succeeds because $C_6F_5$ has inductive effects that increase the oxidation state of the S atom for hypervalency. Another way (kinetic stabilization) is to avoid decomposition of these thermodynamically unstable compounds by introducing suitable chelating ligands, such as 2,2′-biphenylylene first reported by Furukawa et al. (Scheme 2) [67, 68]. This consideration may also be interpreted in light of the "five-membered ring effect" suggested by Martin et al. [69].



**Scheme 2** The tetracoordinated sulfurane $(C_{12}H_8)_2S$

Persulfuranes with all carbon ligands had not been known until very recently, when the novel structure of bis(2,2′-biphenylylene)dimethylpersulfurane $(C_{12}H_8)_2(CH_3)_2S$ was synthesized experimentally, an important achievement by Sato et al. [70]. Those authors determined that this molecule has a distorted octahedral geometry and a *cis* configuration with respect to the methyl ligands (see Scheme 3). X-ray crystallographic analysis was used to determine the structure of this novel compound [70]. The authors also performed theoretical studies in order to understand the bonding nature of this species, and they explained that the *trans* isomer may be hindered by the unfavorable repulsive interaction of the two nearby biphenylylene ligands. However, *trans* isomers have been reported for related hypervalent species [71], and a possible



**Scheme 3** *Cis* (left) and *trans* (right) structures for $(C_{12}H_8)_2(CH_3)_2S$

nondissociative mechanism for the isomerization between the *cis* and *trans* configurations was suggested by Bailar long ago [72]. In the present article, we consider the observed *cis* structure of $(C_{12}H_8)_2(CH_3)_2S$ theoretically and compare our theoretical results with experiment. In addition, we explore the possibility of the existence of *trans* isomers and their stability in both thermodynamic and kinetic senses. We further predict mechanisms for the isomerization processes deduced.

## 4 Theoretical methods

Two density functional (DFT) methods were used in the present research. The first is B3LYP, which arises from Becke's three-parameter hybrid functional (B3) and the Lee–Yang–Parr (LYP) correlation functional [73, 74]. The second method is BP86, which combines Becke's 1988 exchange functional (B) with Perdew's 1986 gradient corrected correlation functional (P86) [75, 76].

Standard double-$\zeta$ plus polarization (DZP) basis sets were used in this research. For carbon and sulfur, these basis sets are constructed by adding one set of pure spherical harmonic *d* polarization functions with orbital exponents $\alpha_d(C) = 0.75$ and $\alpha_d(S) = 0.70$ to the Huzinaga–Dunning–Hay standard contracted DZ sets [77–79], designated as $(9s5p1d/4s2p1d)$ for carbon, and $(12s8p1d/6s4p1d)$ for sulfur. The DZP basis sets for hydrogen is composed of the standard Huzinaga–Dunning double-$\zeta$ set [77, 79] plus one set of pure spherical harmonic *p* polarization functions with $a_p(H) = 0.75$, designated as $(4s1p/2s1p)$. There are 523 basis functions in the present DZP basis set for the molecule bis(2,2′-biphenylylene)dimethylpersulfurane. Natural bond orbital (NBO) analyses [80] are performed at the same levels of theory to investigate the bonding character of these compounds. All computations were carried out with the GAUSSIAN 03 program package [81].

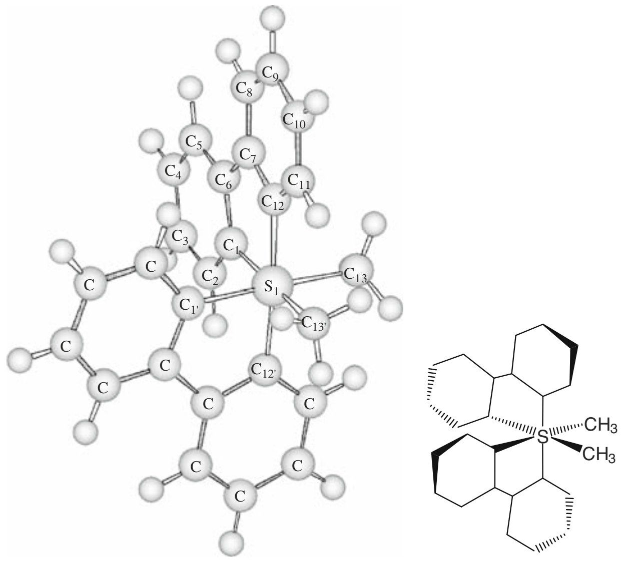


**Fig. 1** The optimized equilibrium geometry for *cis* $(C_{12}H_8)_2(CH_3)_2S$ ($C_2$ symmetry, $^1A$)

**Table 1** Structures of $(C_{12}H_8)_2(CH_3)_2S$ bis(2,2′-biphenylylene) dimethyl persulfurane

| | $r(S_1–C_{13})$ | $r(S_1–C_{12})$ | $r(S_1–C_1)$ | ∠ (C–S–C) |
|---|---|---|---|---|
| B3LYP | | | | |
| *cis* | 1.933 | 1.948 | 1.947 | 85.1°–92.7° |
| *trans*-1 | 1.927 | 1.966 | 1.966 | 83.6°–96.4° |
| *trans*-2 | 1.943 | 1.981 | 1.977 | 84.1°–98.4° |
| BP86 | | | | |
| *cis* | 1.943 | 1.957 | 1.956 | 85.1°–92.8° |
| *trans*-1 | 1.937 | 1.975 | 1.975 | 83.7°–96.3° |
| *trans*-2 | 1.955 | 1.989 | 1.985 | 83.9°–98.3° |
| Exp[a] | | | | |
| *cis* | 1.891 | 1.919 | 1.936 | 85.53(8)°–93.80(10)° |

The S–C bond lengths (Å) and the bond angle range of C–S–C angles predicted by the B3LYP and BP86 methods. The experimental *cis* structure from Ref. [70] is included for comparison

[a] Ref. [70]

## 5 Results and discussion

Our DFT optimized structure for the *cis* form of $(C_{12}H_8)_2(CH_3)_2S$ is predicted to have $C_2$ symmetry (shown in Fig. 1). It is a distorted octahedral structure, in agreement with experiment [70]. Both the B3LYP and BP86 methods predict the *cis* form to be a genuine minimum on the potential hypersurface with a lowest vibrational frequency of 44 or 41 $cm^{-1}$ by the B3LYP and BP86 methods, respectively (Table 1).

The geometrical parameters predicted by the two DFT methods are quite similar (Table 1) and also close to the experimental values. For the *cis* configuration, the B3LYP bond lengths $S–C_{13}$, $S–C_{12}$, and $S–C_1$ are 1.933, 1.948, and 1.947 Å, respectively, while those from BP86 are 1.943, 1.957, and 1.956 Å, respectively. The differences between B3LYP and BP86 structures are small (<0.01 Å) and consistent. Compared to the experimental S–C bond distances [70], the theoretical S–C bond lengths are somewhat longer, by 0.01–0.04 Å (B3LYP) or 0.02–0.05 Å (BP86). The 12 C–S–C bond angles of the *cis* configuration vary from 85.1° to 92.7° (B3LYP) or from 85.1° to 92.8° (BP86), indicating a structure only slightly distorted from octahedral symmetry. The largest angle predicted by our DFT methods is $C_{12}–S–C_{13}$ (92.8°), while the smallest is $C_1–S–C_{12}$ (85.1°). These values are in good agreement

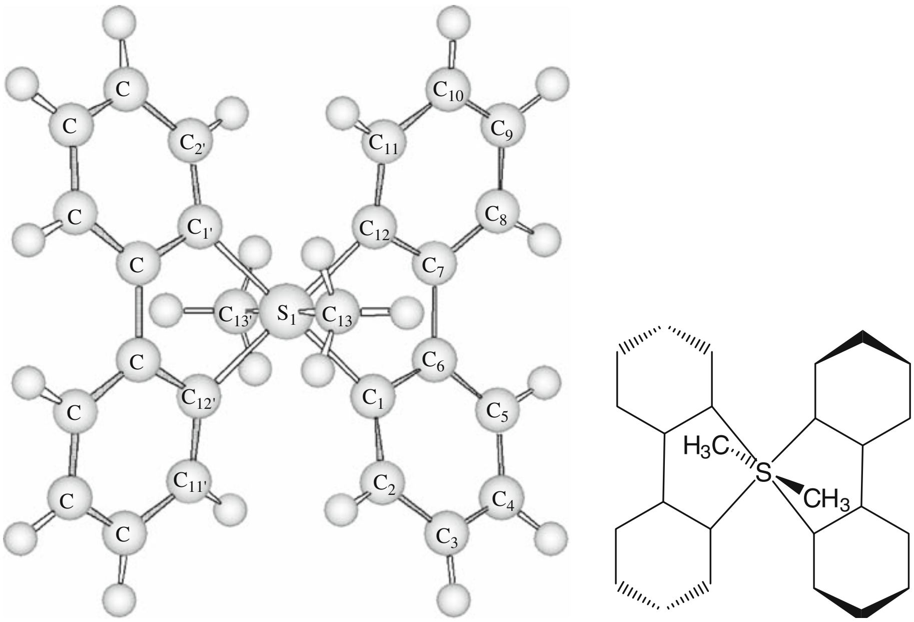


**Fig. 2** The optimized equilibrium geometry for *trans*-1 $(C_{12}H_8)_2(CH_3)_2S$ ($C_{2h}$ symmetry, $^1A_g$)

with the experimental C–S–C angles (93.8°–85.5°, in Table 1) [70].

While the global minimum *cis* configuration has a normal steric arrangement, the expected *trans* configuration will leave the two biphenylylene ligands uncomfortably close, since these biphenylylene ligands would be in the same plane for an octahedral arrangement. To decrease steric repulsive effects, one possible *trans* structure has oppositely directed bent biphenylylene ligands. We name this configuration *trans*-1 (Fig. 2). Our theoretical results show that the *trans*-1 configuration (with $C_{2h}$ symmetry) is a genuine minimum on the potential energy hypersurface predicted by both the B3LYP and BP86 methods. The lowest harmonic vibrational frequency for *trans*-1 is 34 $cm^{-1}$ (B3LYP) or 33 $cm^{-1}$ (BP86). The S–$C_{13}$ (carbon in methyl group) distance for *trans*-1 is predicted to be 1.927 Å (B3LYP) or 1.937 Å (BP86). The S–$C_1$ distance (carbon atom in biphenylylene, and S–$C_{12}$ by symmetry) is 1.966 Å (B3LYP) or 1.975 Å (BP86). Compared with the *cis* isomer, the S–$C_{13}$ distance of the *trans*-1 isomer is slightly shorter (by <0.01 Å), and the S–$C_{12}$ and S–$C_1$ distances of the *trans*-1 isomer are slightly longer (by 0.02 Å). For the *trans*-1 isomer, the C–S–C bond angles around the central sulfur atom are in the range of 83.6° to 96.4° (B3LYP) or 83.7° to 96.3° (BP86). This indicates that the distortion from the perfect $O_h$ structure is slightly larger than that for the *cis* isomer, probably caused by the bending of the two biphenylylene ligands. For each bent biphenylylene ligand in the *trans*-1 structure, the dihedral angle between the two phenyl rings is 151.5° (B3LYP) or 151.6° (BP86). With this bending, the distance between the two hydrogen atoms on $C_{2'}$ and $C_{11}$ (Fig. 2) is 2.080 Å (B3LYP) and 2.084 Å (BP86), which is sufficiently distant to avoid the strong repulsive interaction (suggested by Sato et al. [70]) between the two biphenylylene ligands.

As expected, the strain incurred by the bending of the biphenylylene ligands raises the energy. Our theoretical results (Table 3) show that the energy difference between the *trans*-1 structure and the *cis* structure is 17 (B3LYP) or 15 kcal/mol (BP86). This is undoubtedly one reason the *trans* structure was not observed in the experiments [70].

The single crystal of the *cis* compound in Sato's experiment was recrystallized from $CHCl_3$ solution [70]. From our results, the *cis* configuration has a dipole moment of 0.39 debye (B3LYP) or 0.34 debye (BP86), while the *trans*-1 configuration has a vanishing dipole moment by symmetry. Since $CHCl_3$ is a polar solvent, it should be easier to dissolve the *cis* isomer than the *trans*-1 isomer. This may be another reason why only the *cis* isomer was observed in Sato's experiments.

There is another possible *trans* structure, with both biphenylylene ligands planar, but the two ligands, not coplanar to avoid the steric repulsive interaction. This *trans* (designated *trans*-2 in Fig. 3) configuration of $(C_{12}H_8)_2(CH_3)_2S$ has $C_2$ symmetry, and it is predicted to be another genuine minimum. The vibrational frequency analysis shows all real vibrational frequencies, with the lowest being 50 $cm^{-1}$ (B3LYP) or 48 $cm^{-1}$ (BP86).

For the *trans*-2 isomer, the $S_1$–$C_{13}$, $S_1$–$C_{12}$, and $S_1$–$C_1$ distances are 1.943, 1.981, and 1.977 Å, respectively (B3LYP), or 1.955, 1.989, and 1.985 Å, respectively (BP86). The two DFT methods predict similar S–C

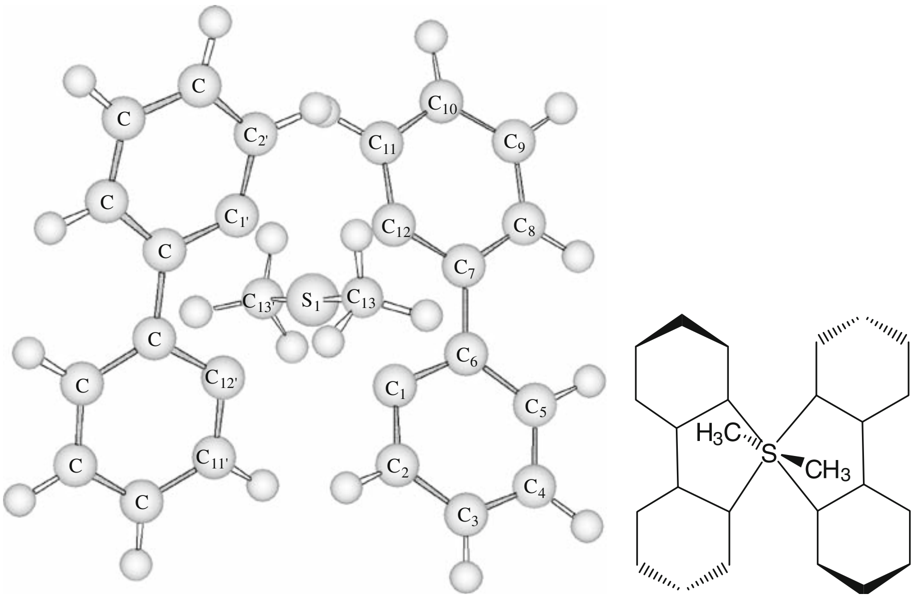


**Fig. 3** The optimized equilibrium geometry for *trans*-2 $(C_{12}H_8)_2(CH_3)_2S$ ($C_2$ symmetry, $^1A$)

distances within ~0.01 Å. Compared with those of *trans*-1, the S–C distances for *trans*-2 are slightly longer by ~0.015 Å (B3LYP). For the *trans*-2 isomer, the C–S–C bond angles around the central sulfur atom have a range of 84.1° to 98.4° (B3LYP) or 83.9° to 98.3° (BP86), indicating slightly more *trans*-2 distortion from the $O_h$ arrangement than for the *trans*-1 isomer. With more geometric strain, the *trans*-2 structure lies slightly higher in energy than *trans*-1 (Table 3). The energy for the *trans*-2 structure compared to the *cis* isomer is predicted to be 19.2 kcal/mol (B3LYP) or 17.5 kcal/mol (BP86).

Natural bond orbital (NBO) analyses [80] show (Table 2) that the natural atomic charge of the central sulfur atom is positive (about +1.0), while the carbon atoms around the sulfur atom are negative (primarily the carbon atoms of methyl groups). For the *cis* configuration, the natural atomic charges of S, $C_1$, $C_{12}$, $C_{13}$ are predicted to be +1.07, −0.16, −0.18, and −0.79, respectively (B3LYP), or +1.03, −0.16, −0.17, and −0.81, respectively (BP86). According to the NBO analyses, the occupancies of the 3*s*, 3*p*, and 3*d* natural atomic orbitals of the sulfur atom in the *cis* configuration are 1.28, 3.55, and 0.10, respectively (B3LYP), or 1.30, 3.58, and 0.09, respectively (BP86). This shows that the hypervalent 3c–4e bonds for the sulfur atom are mainly constructed from 3*s* to 3*p* orbitals, with almost no *d* orbital contributions.

For the *trans*-1 structure, the atomic charges for S, $C_1$, $C_{12}$, $C_{13}$ are +1.04, −0.17, −0.17, and −0.76, respectively, by B3LYP, or +1.00, −0.16, −0.16, and −0.79, respectively, by BP86. For the *trans*-2 configuration, the analogous results are +1.02, −0.17, −0.16 and −0.75, respectively, by B3LYP, or +0.98, −0.16, −0.15 −0.77, respectively, by BP86. All the values are comparable with those for the cis isomer, indicating no major bonding pattern changes among these three isomers. The natural atomic orbitals of the sulfur atom in the *trans*-1 and *trans*-2 configurations (Table 2) are also similar to those for the *cis* configuration.

**Table 2** The natural atomic charges and the occupancies of the atomic orbitals of the sulfur atom in $(C_{12}H_8)_2(CH_3)_2S$

| | Natural atomic charges | | | | Occupancies | | |
|---|---|---|---|---|---|---|---|
| | $S_1$ | $C_1$ | $C_{12}$ | $C_{13}$ | 3*s* | 3*p* | 3*d* |
| B3LYP | | | | | | | |
| *cis* | +1.070 | −0.164 | −0.180 | −0.788 | 1.28 | 3.55 | 0.10 |
| *trans*-1 | +1.041 | −0.167 | −0.167 | −0.762 | 1.29 | 3.57 | 0.10 |
| *trans*-2 | +1.024 | −0.165 | −0.163 | −0.751 | 1.31 | 3.57 | 0.09 |
| BP86 | | | | | | | |
| *cis* | +1.026 | −0.155 | −0.172 | −0.811 | 1.30 | 3.58 | 0.09 |
| *trans*-1 | +0.998 | −0.158 | −0.158 | −0.785 | 1.31 | 3.60 | 0.09 |
| *trans*-2 | +0.982 | −0.156 | −0.153 | −0.773 | 1.33 | 3.60 | 0.08 |
| Ref. [70] | | | | | | | |
| *cis* | +1.265 | −0.175 | −0.189 | −0.718 | 1.27 | | 0.09 |

The previous theoretical results (B3LYP/6-311 + G**) from Ref. [70] are also listed for comparison

To further explore the stabilities of the three isomers, the appropriate transition states were found with the BP86 method. The first transition state TS-1 with $C_2$ symmetry (see Fig. 4) is a Bailar twist [72] between the *cis* and *trans*-2 configurations. Its sole imaginary frequency is 130*i* cm$^{-1}$, and our intrinsic reaction coordinate (IRC) confirms that the related normal mode connects the *cis* and

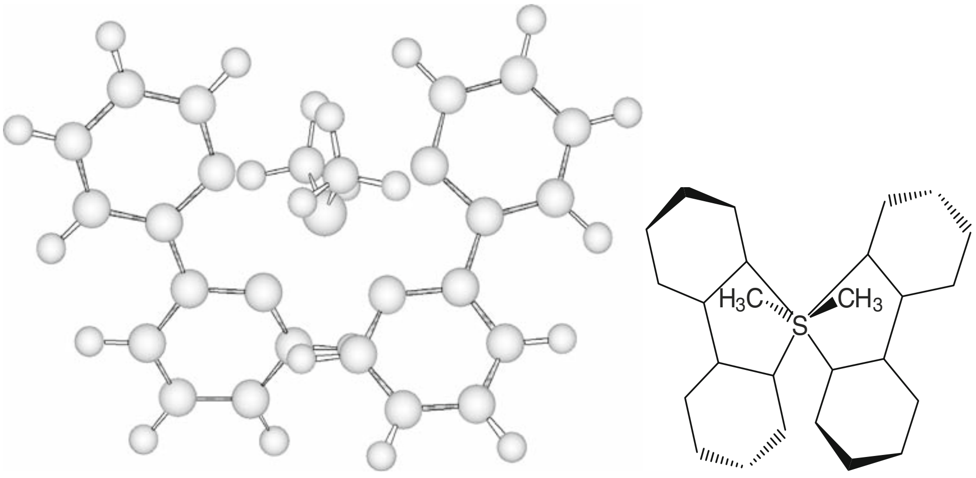


**Fig. 4** The optimized geometry for the transition state (TS-1) between the *cis* and *trans*-1 isomers

**Table 3** The lowest vibrational frequencies ($v_1$, $cm^{-1}$), total energies ($E_t$, hartree), relative energies ($\Delta E$, kcal/mol), orbital energies of HOMO and LUMO (in hartree), and zero point vibrational energy (ZPVE, kcal/mol) of all the optimized $(C_{12}H_8)_2(CH_3)_2S$ structures with the B3LYP and BP86 methods

| | $v_1$ | $E_t$ | $\Delta E$ | HOMO | LUMO | ZPVE |
|---|---|---|---|---|---|---|
| B3LYP | | | | | | |
| *cis* | 44 | −1402.10832 | 0.0 | −0.2136 | −0.0443 | 249.8 |
| *trans*-1 | 34 | −1402.08173 | 16.7 | −0.2145 | −0.0446 | 249.2 |
| *trans*-2 | 50 | −1402.07772 | 19.2 | −0.2086 | −0.0419 | 249.4 |
| BP86 | | | | | | |
| *cis* | 41 | −1402.13426 | 0.0 | −0.1891 | −0.0728 | 242.0 |
| *trans*-1 | 33 | −1402.10969 | 15.4 | −0.1893 | −0.0740 | 241.5 |
| *trans*-2 | 48 | −1402.10634 | 17.5 | −0.1840 | −0.0710 | 241.6 |
| TS-1 | 130*i* | −1402.03764 | 60.6 | −0.1674 | −0.0807 | 239.8 |
| TS-2 | 107*i* | −1402.10281 | 19.7 | −0.1883 | −0.0713 | 241.2 |

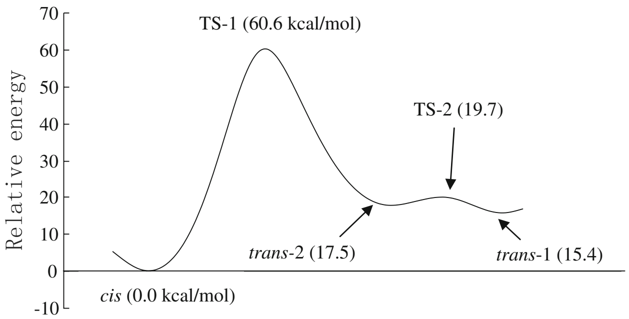


**Fig. 5** The potential energy sketch of stationary point structures for $(C_{12}H_8)_2(CH_3)_2S$

*trans*-2 configurations. The unimolecular barrier height approaching TS-1 from the *cis* side is as high as 60.6 kcal/mol, while that from the *trans*-2 side is 43.1 kcal/mol (Table 3, Fig. 5). This barrier is sufficiently high to make both *cis* and *trans*-2 structures kinetically stable. This former *cis–trans* barrier (60.6 kcal/mol) is slightly lower than the S–C bond dissociation energy (65–73 kcal/mol [82, 83]).

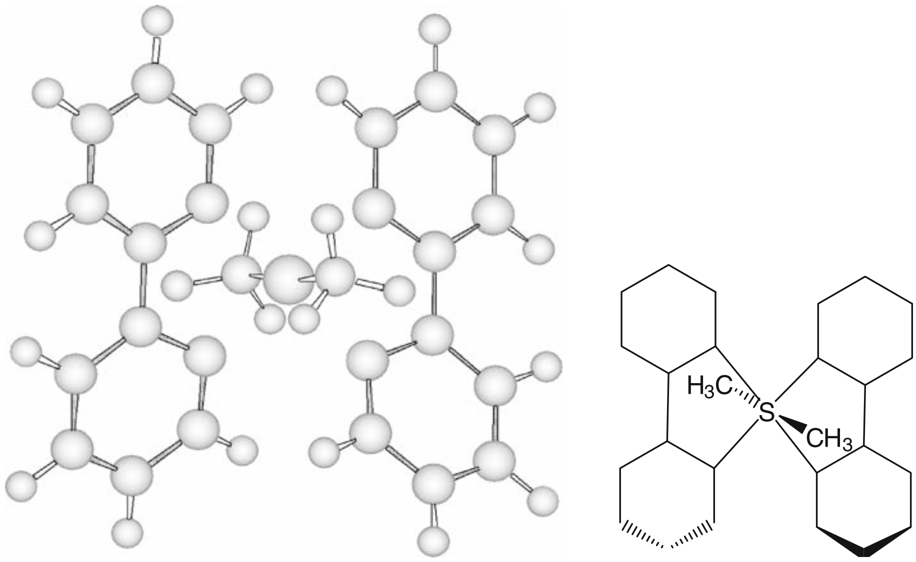
Another transition state (TS-2, $C_2$ symmetry, Fig. 6) connects the *trans*-1 and *trans*-2 configurations, which is confirmed by an IRC study at the same theoretical level. The sole imaginary frequency for TS-2 is 107*i* $cm^{-1}$. The barrier height of TS-2 is quite low, 2.2 kcal/mol from the *trans*-2 side and 4.3 kcal/mol from the *trans*-1 side, suggesting that these two *trans* conformations can be exchanged easily. However, transit to the *cis* structure is difficult energetically.

## 6 Summary

In this Account, we begin by briefly describing the concept of hypervalent molecules, a term introduced by Musher in 1969 [6]. We continue by reviewing our own research of the past 35 years on sulfuranes and persulfuranes. From that point we proceed to a detailed theoretical study related to the most important experimental sulfurane discovery of the past decade, the synthesis of a persulfurane with all carbon ligands.

The geometries of three minima (*cis*, *trans*-1, and *trans*-2) for the hypervalent bis(2,2′-biphenylylene)dimethylpersulfuranes $(C_{12}H_8)_2(CH_3)_2S$ were fully optimized using both hybrid and pure density functional theory methods (B3LYP and BP86). The *cis* structure is the global minimum, and the theoretical geometric parameters are in good agreement with the experimental crystal structure. The *trans*-1 and *trans*-2 structures, which have not observed experimentally, lie in energy above *cis* structure by <20 kcal/mol, due to the strain associated with biphenylylene bending. We also located transition states connecting

**Fig. 6** The optimized geometry for the transition state (TS-2) between the *trans*-2 and *trans*-1 isomers



these new equilibrium structures, and discuss kinetic and thermodynamic stabilities.

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