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Theoretical analysis of the internal rotation and determination of molecular structures of HSSH, HSSF and FSSF

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Summary. A detailed investigation of the internal rotation of hydrogen persulfide and fluoro-derivatives is presented. High quality potential functions containing only three and four parameters were determined through a very simple interpolation method. Reduced torsional potentials are defined and used to assess the quality of the interpolated functions. Equilibrium structures and barriers to internal rotation reported here are in close agreement with the available experimental data. High barrier heights and the comparative analysis of structural parameters of all three molecules indicate significant π bonding through the mechanism of hyperconjugation.

Key words: Internal rotation—Torsional potential—Rotational isomerism—Hydrogen persulfide

1. Introduction

In the last few years, many theoretical and experimental works on the characteristic features of the internal rotation of hydrogen persulfide and related molecules have appeared. They report in general, molecular structure, barrier heights, rotational spectrum and related matters concerning the dynamics of the internal rotation. In contrast to the large amount of data for the parent molecule HOOH, much less information is available for HSSH. Only very recently an experimentally determined potential function for the torsional motion of HSSH was reported [1]. Compounds containing S–S and S–X bonds serve as model for the S–S linkage in proteins and provide a starting point for understanding the structure of many systems. Knowledge of the factors that influence properties such as bond lengths, bond strengths and conformations of disulfides is therefore important to several areas of chemistry and biochemistry.

The structure of hydrogen persulfide has been investigated by microwave spectroscopy and by electron diffraction methods [1, 2]. The molecule presents two maxima at the *cis* and *trans* conformations (dihedral angle $\alpha = 0°$ and $\alpha = 180°$, respectively). A gauche stable isomer is found around midway between both maxima. The experimentally determined geometrical parameters for the stable isomer were found to be: $r(\text{S–S}) = 2.055$ Å, $r(\text{S–H}) = 1.327$ Å, SSH = 91.3° and a dihedral angle of $\alpha_0 = 90.4°$ [2], (in [1] the dihedral angle reported is 87.7°). However a recent study by Harmony et al. quotes $r(\text{S–S}) = 2.058$ Å, $r(\text{S–H}) = 1.345$ Å, SSH = 98.1° and $\alpha_0 = 90.8°$ [3]. The most important discrepancy between the two sets of experimental data appears in the SSH bond angle for which the reports differ by more than 7%. Concerning the potential governing the internal rotation, the experimental information is meager. Only very recently, Herbst and Winnewisser [1] determined the *cis* and *trans* barrier heights for HSSH from a variety of milimeter-wave and far-infrared spectral data.

From the theoretical viewpoint few studies based on *ab initio* SCF-MO calculations of the torsional potential in HSSH have been published recently [4, 5]. Most of them use a basis of roughly double-ζ plus polarization orbitals on the sulfur atoms. There is a general agreement that the use of an unpolarized basis should give a long unrealistic S–S distance. Hinchliffe [4] optimized the geometry of gauche-HSSH and reported 2.081 Å for the S–S distance, 1.356 Å for the S–H distance, 98.3° for the HSS angle and 91.7° for the dihedral angle. Concerning the torsional barriers, the most sophisticated treatments report *cis* and *trans* barrier heights which are in close agreement with experimental estimations [5].

In this paper we use an interpolation procedure to get accurate torsional potential functions for XSSX (X = H, F). The interpolation method was used with success in determining torsional potential functions of different molecules from a reduced number of computed energies [6–9]. However, in the present study, the formalism used is slightly different since we explore the potential function starting from the knowledge of properties associated to the unstable conformations. Although there have been several publications reporting calculations on molecules of the type XSSX, in the present paper we analyse the torsional potential in more detail than other authors have done. We have determined high-quality potential functions based on *ab initio* calculations at the STO-NG/S* level (hereafter referred to as MN*, $N = 3, 6$). We have introduced reduced torsional potential functions to quantify the effect of the quality of the SCF calculations on the final results. Although our results concerning the barrier heights are somewhat higher than the experimental estimates, there is an overall agreement within a reasonable degree of uncertainty.

Despite the relatively small basis set used in our calculations, we have found that the S–S bond distance decreases in going from HSSH to FSSF, in agreement with experimental observations. Our results show that this behaviour can be explained in terms of the hyperconjugative mechanism of π bonding.

In Sect. 2 of this paper we describe the interpolation method. Details of the calculations are presented in Sect. 3. Torsional potentials containing three and four parameters are presented and discussed in Sect. 4. An analysis of the geometry changes during the internal rotation is given in Sect. 5. Section 6 contains our concluding remarks.

2. Theoretical considerations

The potential function $V(\alpha)$ hindering the internal rotation of XSSX (X = H, F) can be expressed in terms of a limited cosine expansion as follows:

$$V(\alpha) = V_0 + \sum_{j=1}^{j_{\max}} V_j \cos(j\alpha), \tag{1}$$

where $j_{\max} = 3$ is the number of independent input data used to fit $V(\alpha)$. Usually it is fitted to observed data associated with the stable conformations; these data are the torsional force constants and the energy difference between the stable isomers [7]. Unfortunately, in the present case no information characterizing the stable conformation is available. The only data we have are the positions of the two energy maxima that are located at $\alpha = 0°$ and $\alpha = 180°$. Fortunately the theoretical calculations permit one to investigate molecules and molecular conformations that are inaccessible to direct experimental study. Consequently we shall explore the possibility of getting torsional potential functions starting from a knowledge of the properties associated with the unstable conformations. To do so we shall apply the interpolation method we have already used in our previous studies [7–9].

Let us first define local potentials that describe the region of the maxima accurately. From these potentials we shall obtain reference properties to be used as input data in the interpolation procedure. Local potentials can be conveniently expanded in Taylor series around the maxima. The harmonic approximation leads to the following truncated expression for the local potentials:

$$V^{(m)}(\alpha) = V^{(m)}(\alpha_m) + \tfrac{1}{2}K_m[\alpha - \alpha_m]^2 \quad (m = c, t). \tag{2}$$

K_m is the second derivative of $V^{(m)}(\alpha)$, and $V^{(m)}(\alpha_m)$ is an additive constant. The parameter K_m can be determined from calculated energies in the vicinity of the maxima:

$$K_m = \frac{2\{V^{(m)}(\alpha_i) - V^{(m)}(\alpha_m)\}}{(\alpha_i - \alpha_m)^2} \quad (m = c, t; i \neq m), \tag{3}$$

where α_i denotes a conformation reasonably close to α_m [7, 8].

Another equation used to get the potential parameters comes from the energy difference (ΔV_{ct}) between the maxima:

$$\Delta V_{ct} = V(\alpha_c) - V(\alpha_t) = \sum_{j=1}^{3} V_j[\cos(j\alpha_c) - \cos(j\alpha_t)]. \tag{4}$$

Knowing the K_m's and ΔV_{ct} values, the potential parameters V_1, V_2 and V_3 of

Eq. (1) are determined through the following relations:

$$V_1 = \tfrac{1}{2}\Delta V_{ct} - \tfrac{1}{16}[K_t - K_c - \Delta V_{ct}], \tag{5a}$$

$$V_2 = -\tfrac{1}{8}[K_t + K_c], \tag{5b}$$

$$V_3 = \tfrac{1}{16}[K_t - K_c - \Delta V_{ct}] \tag{5c}$$

and

$$V_0 = [V_1 - V_2 + V_3]. \tag{5d}$$

The position (α_0) of the stable conformation is estimated by solving $(dV/d\alpha) = 0$. This yields:

$$\cos\alpha_0 = \frac{1}{6V_3}[-V_2 - [V_2^2 - 3V_3(V_1 - 3V_3)]^{1/2}]. \tag{6}$$

It is worth mentioning that since the resulting potential function is based upon data associated to the transition states, estimates of the location and predicted properties of the stable conformation might not be accurate enough. An improved description of the potential well can be obtained by including one more parameter in the potential function. To do so we use the optimized energy of the stable conformation as a fourth input datum. The value of α_0 that came out of Eq. (6) is therefore considered as a first guess of the location of the stable isomer. *Ab initio* calculations will provide both the optimized α_0 value and the corresponding energy to be used as the fourth external datum. This entails a change in the V_2 parameter which is now corrected to give:

$$V_2^r = \frac{1}{A}[4\Delta V_c^{\ddagger} - 2\Delta V_{ct} + 4[V_1\cos\alpha_0 + V_3\cos 3\alpha_0] - V_2(1 - \cos 4\alpha_0)], \tag{7}$$

where $A = 2(\cos 2\alpha_0 - 1)^2$ and $\Delta V_c^{\ddagger}$ comes from the *ab initio* optimization of all structural parameters of the gauche stable isomer, including the torsional angle. The new parameter, V_4, is expressed as the difference between the old and new two-fold parameters:

$$V_4 = \tfrac{1}{4}[V_2 - V_2^r]. \tag{8}$$

Therefore, if the quality of $V(\alpha)$ is determined by the accuracy of the predicted value of the potential barriers, then V_4 can be regarded as a measure of the quality of the original function.

3. Calculations

In this paper we are mainly interested in establishing the quality of the interpolation procedure for molecules presenting a gauche stable conformation. In illustrating this point we choose to use a relatively modest level of approximation in the *ab initio* calculations. It has been shown in a variety of sulfur containing molecules that minimal basis sets including *d* polarization functions on the sulfur atom could lead to quantitatively reasonably results concerning relative energies and molecular structures [6, 7, 10]. For this reason we decided to use a minimal STO-NG basis set ($N = 3, 6$) plus *d* polarization orbitals on the sulfur atoms in our *ab initio* calculations along the torsional mode of HSSH, HSSF and FSSF. In all calculations presented here geometries were fully optimized at the M3* level.

To assess the quality of the interpolation method we shall first analyse in detail the potential function hindering the internal rotation of HSSH. The quality of the interpolated potential function will be checked through comparison of a number of predicted and calculated energies. To this effect we performed systematic M3* calculations starting from both transition states and stepping down every ten degrees; this is from $\alpha = 0°$ to $\alpha = 80°$ and from $\alpha = 180°$ to $\alpha = 100°$ in the *cis* and *trans* regions, respectively. The results of these calculations are summarized in Table 1 and discussed in the next section. On the other hand, to see the effect of the number of Gaussian primitives on the interpolated function, additional calculations were carried out on HSSH using the M6* basis set.

Once the interpolation procedure was tested and the quality of the interpolated function established for HSSH, we were able to get torsional potential functions for HSSF and FSSF from a minimum number of energy-points. In all three cases input parameters used to determine $V(\alpha)$ were calculated through Eq. (3) using energy-points at ($\alpha = 0°, 10°$) for K_c and ($\alpha = 170°, 180°$) for K_t, respectively.

Table 1. Calculated M3* energies for HSSH

α/ °	E/ (Hartrees)	$V(\alpha)$/ (kcal/mol)
0-*cis*	−787.569762	3.2994
10	−787.570331	2.9424
20	−787.571959	1.9208
30	−787.574414	0.3803
40	−787.577365	−1.4715
50	−787.580429	−3.3942
60	−787.583230	−5.1519
70	−787.585437	−6.5368
80	−787.586800	−7.3921
100	−787.586601	−7.2672
110	−787.585195	−6.3849
120	−787.583239	−5.1575
130	−787.581066	−3.7939
140	−787.578998	−2.4962
150	−787.577270	−1.4119
160	−787.576015	−0.6244
170	−787.575267	−0.1550
180-*trans*	−787.575020	0.0

4. Torsional potentials

4.1. HSSH: Comparison with experimental results

Input data K_c, K_t and ΔV_{ct} for HSSH together with the resulting potential parameters are given in Table 2. We also include in the table potential parameters based on experimental data, determined recently by Herbst and Winnewisser [1]. In view of the difference between theoretical and experimental values of ΔV_{ct}, we should not expect our results to be numerically very close to the experimental ones. In fact, our potential parameters systematically overestimate the corresponding experimental value; however, the overall agreement between theoretical and experimental results is qualitatively good, despite the approximation involved in our interpolation method and the small basis sets employed in the SCF calculations.

It is clear that potential functions defined through quite different data will show at best a qualitative agreement. However, good quantitative agreement between theoretical and experimental results is obtained when we compare reduced potential functions. Differences appearing in the theoretical and experimental ΔV_{ct} values suggest that this should be one natural reducing parameter, and reduced potential functions are therefore defined as $V^*(\alpha) = V(\alpha)/\Delta V_{ct}$. Reduced parameters $V_n^* = V_n/\Delta V_{ct}$ and properties $((\Delta V_c^{\ddagger})^* = \Delta V_c^{\ddagger}/\Delta V_{ct}$, $(\Delta V_t^{\ddagger})^* = \Delta V_t^{\ddagger}/\Delta V_{ct})$ are shown in Table 3. It is evident that theoretical values, specially the refined M3* set, are now in close agreement with the experimental ones. This shows that our interpolation method and the procedure used to get the

Table 2. M3* and M6* input data (K_c, K_t and ΔV_{ct}), torsional potential parameters (in kcal/mol) and resulting characteristic properties for the internal rotation of HSSH

	M3*	Refined M3*[b]	M6*	Refined M6*[b]	Experimental[c]
K_c	−23.4392		−23.3998		
K_t	−10.1767		−10.4262		
ΔV_{ct}	3.2994		3.1670		2.5344
V_0	−2.5523	−2.8791	−2.6448	−2.9674	−2.1942
V_1	1.0270	1.0270	0.9706	0.9706	0.8097
V_2	4.2020	4.6378	4.2283	4.6584	3.4613
V_3	0.6227	0.6227	0.6129	0.6129	0.4574
V_4		−0.1090		−0.1075	
σ	0.3057	0.0447			
α_0	87.19°	88.84°	87.12°	88.78°	87.7°
$k(\alpha_0)$[a]	0.1216	0.1432	0.1224	0.1436	0.0992
$\Delta V_c^{\ddagger}$	10.0744	10.9381	10.0621	10.9141	8.2003
$\Delta V_t^{\ddagger}$	6.7750	7.6387	6.8951	7.7471	5.6659

[a] Force constants in mdyn Å/rad^2

[b] Numerical results for α_0, $\Delta V_c^{\ddagger}$ and $\Delta V_t^{\ddagger}$ correspond to the optimized value

[c] From [1]

Table 3. Theoretical and experimental reduced potential parameters and barriers to internal rotation for HSSH

	M3*	Refined M3*	M6*	Refined M6*	Experimental
V_0^*	−0.7736	−0.8726	−0.8351	−0.9370	−0.8658
V_1^*	0.3113	0.3113	0.3065	0.3065	0.3195
V_2^*	1.2736	1.4056	1.3351	1.4709	1.3657
V_3^*	0.1887	0.1887	0.1935	0.1935	0.1805
V_4^*		−0.0330		−0.0339	
$(\Delta V_c^{\ddagger})^*$	3.0534	3.3152	3.1772	3.4462	3.2356
$(\Delta V_t^{\ddagger})^*$	2.0534	2.3152	2.1772	2.4462	2.2356

input parameters K_c and K_t lead to realistic potential functions, in agreement with previous observations [7–9]. On the other hand, we conclude that a good estimate of ΔV_{ct} is essential if one is to obtain high quality numerical results. This would be a good criteria to choose the level of approximation in the SCF scheme.

Reduced potential functions should be important in rationalizing theoretical and experimental data on internal rotations for quite different systems. Calculated potential functions for HSSH can get very close to the experimentally determined function if we scale them by using the multiplicative factor $\Delta V_{ct}(\mathrm{exp})/\Delta V_{ct}(\mathrm{calc})$. Furthermore, our analysis allows us to make a guess concerning the numerical value of the parameter V_4, that was not included in the representation of the experimental potential [1] due to the shortage of spectral frequencies. We expect this value be around −0.08 kcal/mol.

4.2. *Barriers to internal rotation and refined potential functions*

Potential barriers are mainly determined by the V_2 parameter. In a previous paper [8] we have shown that barrier heights can be estimated through the following approximate formula:

$$\Delta V_c^{\ddagger} \approx 2V_2 + \tfrac{1}{2}\Delta V_{ct}. \tag{9}$$

It can be checked that this formula reproduces the $\Delta V_c^{\ddagger}$ values appearing in Tables 2–4 within an error of less than 1%. Good estimates of barrier heights in terms of the three input data are then obtained through Eq. (9); this equation holds for the case of molecules presenting a gauche stable conformation near $\alpha = 90°$, i.e. around halfway between the transition states.

In Fig. 1 we display the M3* potential curves. To help appreciate the quality of the interpolated functions, we have included in the figure the energy-points given in Table 1. We note that the three-parameter potential function describes the transition state regions quite accurately, but it fails when approaching the stable isomer. In this region, differences between predicted and calculated values come to about 0.8 kcal/mol. Therefore, a more accurate description of the potential well region should be required.

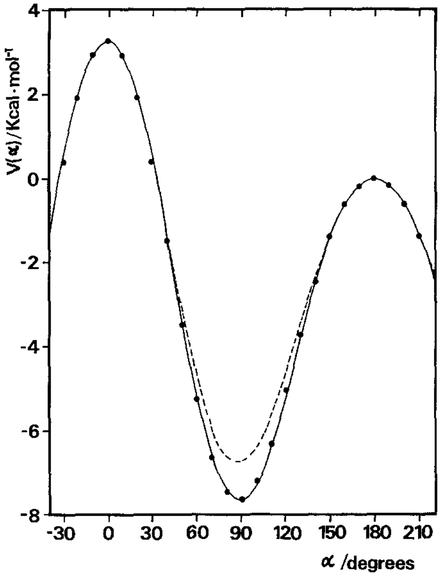

Fig. 1. M3* torsional potential curves for HSSH. The *dashed line* represents the three parameter interpolated function. The *solid line* represents the refined function. The *points* are the *ab initio* values given in Table 1

Refinement of the potential function was carried out following the procedure outlined in Sect. 2 and the refined potential parameters are quoted in Tables 2 and 3. Comparison of the refined and non-refined results shows a remarkable accuracy in the predicted position of the stable conformation. Although the other predicted properties are less accurate, numerical values are within a reasonably expected uncertainty. The corresponding M3* refined potential curve is also shown in Fig. 1. It can be seen that the 4-parameter function is very accurate and therefore it should be used in most applications. The root mean-square deviation σ, also given in Table 2, illustrates this result quantitatively. The numerical value of σ is reduced by a factor of seven when the additional V_4 parameter is included in the representation of $V(\alpha)$.

Combining Eq. (9) with the analogous expression for the refined barrier height as a function of V_2^r, we find that

$$\delta\Delta V_c^{\neq} = |\Delta V_c^{\neq} - \Delta V_c^{\neq}(\text{refined})| = \beta|V_4|, \tag{10}$$

where $\beta = 8$. Due to the approximations involved in the present treatment, specially the fact that the $\Delta V_c^{\neq}$ values appearing in Eq. (10) were calculated for different α_0, we expect that our estimate of β should deviate from the above reference value. Nevertheless, the values of $\beta = \delta\Delta V_c^{\neq}/V_4$ for HSSH approximate the reference value quite well. They are 7.92 and 7.93 for the M3* and M6* calculations, respectively, i.e. within a 1% error. We believe that this small deviation might be mainly associated with structural differences between the isomers at α_0. While $\Delta V_c^{\neq}$(refined) is associated with an optimized reference structure at α_0, no molecular structure can be associated with the interpolated value $\Delta V_c^{\neq}$.

Finally, it is worth mentioning that the comparative analysis of the M3* and M6* results shows that the use of a large number of Gaussian primitives to produce better contracted basis functions does not significantly alter the results obtained using the less expensive M3* basis set.

4.3. HSSH, HSSF and FSSF: comparative analysis

Our investigation was pursued with the study of torsional potentials of two derivatives of HSSH: HSSF and FSSF. This time only the minimum number of calculations necessary to get the input parameters were performed. Input data, together with the resulting potential parameters and properties, are shown in Table 4. We observe the same characteristic features already mentioned for HSSH. Remarkable accuracy in the predicted value of α_0 was achieved in both cases. We also note that the energy difference $\delta \Delta V_c^{\ddagger}$, that comes up to 18% of the optimized value for FSSF, is reflected in the high numerical values of V_4. However, the parameter β remains constant at 7.91 and 7.92 for HSSF and FSSF, respectively.

In Fig. 2 we display the refined potential curves of the molecules under investigation. Comparative analysis of the curves and numerical results show that the values of most parameters associated with HSSF have intermediate values between those corresponding to HSSH and FSSF. It is interesting to note that the parameter V_1 follows the order HSSH > HSSF > FSSF while V_3 behaves in the opposite way. Also we note that for HSSF and FSSF $V_3 > V_1$. These results

Table 4. Input data (K_c, K_t and ΔV_{ct}), potential parameters and torsional properties characterizing the internal rotation of HSSF and FSSF molecules. Results in kcal/mol

	HSSF		FSSF	
	M3*	Refined M3*[b]	M3*	Refined M3*[b]
K_c	−34.7321		−48.8613	
K_t	−21.3842		−29.9129	
ΔV_{ct}	1.9961		2.0601	
V_0	−6.0165	−6.3270	−8.8168	−10.5938
V_1	0.2886	0.2886	−0.0254	−0.0254
V_2	7.0145	7.4286	9.8468	12.2162
V_3	0.7095	0.7095	1.0555	1.0555
V_4		−0.1036		−0.5924
α_0	86.31°	87.41°	85.47°	87.75°
$k(\alpha_0)$[a]	0.2018	0.2230	0.2859	0.4115
$\Delta V_c^{\ddagger}$	15.0866	15.9061	20.8509	25.5427
$\Delta V_c^{\ddagger}$	13.0905	13.9100	18.7908	23.4826

[a] In mdyn Å/rad^2

[b] Numerical results for α_0, $\Delta V_c^{\ddagger}$ and $\Delta V_t^{\ddagger}$ correspond to optimized values. The reference energy at M3* level are:

$E_{\text{HSSF}}(180°) = -885.059999$ Hartrees

$E_{\text{FSSF}}(180°) = -982.541573$ Hartrees

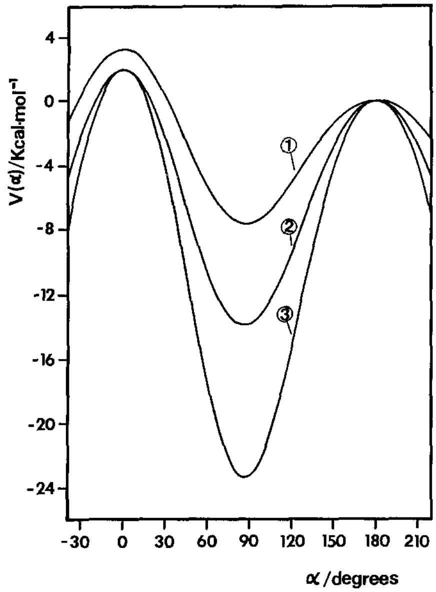

Fig. 2. M3* refined torsional potential curves for HSSH(*1*), HSSF(*2*), and FSSF(*3*)

are explained by analysing the relative values of the input K_c and K_t data and comparing them with the corresponding ΔV_{ct} value. Equations (5a) and (5c) show that $|V_3| > |V_1|$ if $|K_t - K_c| > 5\Delta V_{ct}$ while $|V_3| < |V_1|$ if $|K_t - K_c| < 5\Delta V_{ct}$. Concerning the barriers to internal rotation, they are ordered as follows: FSSF > HSSF > HSSH. This latter result can be explained in terms of hyperconjugative interactions contributing to the π bond character of the S–S bond which is favoured by the electronegativity of fluorine. Evidence for this comes from the observed decrease of the S–S distance from 1.960 Å in HSSH to 1.899 Å in FSSF, as we shall discuss in the next section.

5. Geometry changes during the internal rotation

As explained in Sect. 3, in the case of HSSH we performed full geometry optimization along the torsional angle. All three parameters involved, namely the SSH angle and the S–H and S–S bond distances, pass through extrema at α_0. The SSH angle increases from 96.5° in the *cis* conformation to a maxima of 99.1° at α_0 and then decreases monotonically to reach 93.1° at the *trans* conformation. The S–H bond shows a maximum which is 0.0090 Å and 0.0061 Å larger than the *cis* and *trans* values, respectively. The S–S bond shows a pronounced minimum that is 0.0585 Å and 0.0485 Å smaller than for the *cis* and *trans* conformations, respectively. This large variation in the S–S bond length, which is beyond reasonable errors in the calculations, shows the interaction between the S–H σ bond and the $3p$ orbitals on the other sulfur producing significant π bonding through the mechanism of hyperconjugation.

In Table 5 we display the geometrical parameters for the gauche stable

Table 5. Optimized geometries (in Å and degrees) and associated energetic properties (in kcal/mol) of the stable gauche comformation of XSSX (X = H, F), from *ab initio* calculations

	α_0	r(S–S)	r(S–H)	r(S–F)	(HSS)	(FSS)	$\Delta V_{ct}^{\ddagger}$	$\Delta V_{c}^{\ddagger}$
HSSH M3*	88.84°	1.9602	1.3292		99.07°		3.2994	10.9381
M6*	88.78°	1.9553	1.3248		99.30°		3.1670	10.9141
HSSF M3*	87.41°	1.9343	1.3302	1.5792	100.02°	104.73°	1.9961	15.9061
FSSF M3*	87.75°	1.8988		1.5804		106.59°	2.0601	25.5427

conformations of all three molecules under investigation. The most striking result from Table 5 is the remarkable decrease in the S–S bond length from HSSH to FSSF, confirming the observed strong π bond interaction between the sulfur atoms. In fact, the S–S bond length in FSSF is practically equal to that of the double bond in diatomic sulfur. This effect makes the barrier to internal rotation in HSSF and FSSF much higher than that of HSSH, as shown in Table 5.

6. Concluding remarks

We have presented a detailed analysis of the potential functions hindering the internal rotation of HSSH, HSSF and FSSF. High quality potential functions containing at most four parameters were fully determined through an interpolation procedure that for the first time was applied to molecules presenting a gauche stable conformation. Our results on a series of related molecules show that this procedure gives realistic potential functions within a relatively low computational cost.

We have introduced the idea of reduced torsional potentials to better define the ground on which data coming from different sources may be compared. A scaling factor relating these data was proposed for the HSSH case.

A detailed analysis of the factors determining the relative value of the potential parameters was presented. Also, a simple approximate expression to estimate barrier heights was derived and shown to be both very useful and, in the present case, accurate.

Concerning the numerical results, a good overall agreement between theoretical and the available experimental results was found despite the approximation involved in our procedure, and the limited basis set used in the SCF calculations.

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