

# Analysis of torsional barrier height of HSNO as the simplest S-nitrosothiol

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**Abstract.** Torsional barrier height of thionitrous acid is analysed with Gaussian-2(G2), quadratic complete basis set (CBS-Q) and DFT-B3LYP/CBS-Q (CBS-QB3) methods. In agreement with purely intuitive arguments, it was determined that the *cis* to *trans* barrier height is nearly 5.7–6.3 kcal mol<sup>-1</sup>. In addition, the stability of rotation as function of competing dissociation pathways and also result of natural bond orbital analysis are discussed.

**Keywords.** Gaussian-2 (G2); CBS-Q; CBS-QB3; torsional barrier; thionitrous acid (HSNO).

## 1. Introduction

S-nitrosothiol consists of molecules of biological and medicinal interest, which cause vasodilation of veins and arteries and inhibition of platelet aggregation, through the release of nitric oxide (NO).<sup>1,2</sup> The weakness of S–NO bonds in S-nitrosothiol is clearly evident from their high reactivity.<sup>1,2</sup> Thionitrous acid (HSNO) can be considered as the simplest S-nitrosothiol. There are many reasons behind the significant interest in compounds which include sulphur-containing groups.<sup>3–6</sup> Recently, *ab initio* studies on the electronic structures and relative energies of HSNO isomers have been reported.<sup>7,8</sup> To the best of our knowledge, no comparative computational studies about torsional potential of thionitrous acid have been carried out. In this study, we perform a series of *ab initio* calculations in order to compute the torsional barrier height of HSNO and also discuss the stability of rotation as a function of three competing dissociation pathways. Natural bond orbital (NBO) analysis is also carried out to obtain deeper insight into the reason behind the order of stability for various conformers.

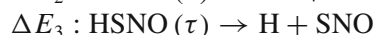
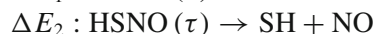
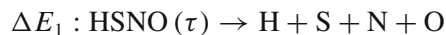
## 2. Computational methods

All Gaussian-2 (G2), quadratic complete basis set (CBS-Q) and DFT-B3LYP/CBS-Q (CBS-QB3), calculations were performed with the GAUSSIAN 98<sup>9</sup> set of

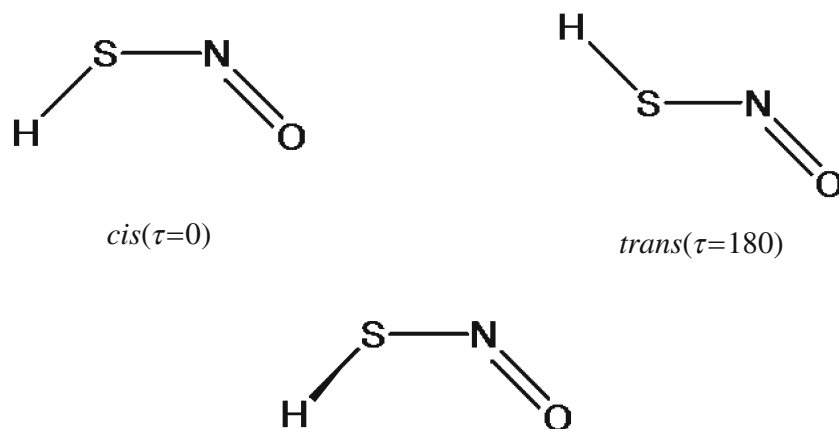
codes. More information about the employed methodology is available in literature.<sup>10</sup> However, essentially the CBS-Q method uses the B3LYP/CBSB7 method to perform geometrical optimizations and frequency computation, while the G2 and CBS-Q methods use MP2 geometries and Hartree-Fock (HF) frequencies, with 6-311G(d), and 6-31G(d') basis sets, respectively.

## 3. Results and discussion

HSNO is planar molecule—its *cis* and *trans* forms are shown in figure 1. In table 1, other species used in our analysis of the decomposition of the HSNO rotation along  $\tau$  are shown. Table 2 shows the computed relative total energies (expressed in kcal mol<sup>-1</sup>) for varying HSNO dihedral angle  $\tau$  in degrees (°). The barrier for conversion of *cis* to *trans* conformer is estimated as the energy difference between the *cis* form and the transition state. In this particular case, the transition state was found to occur at 87 degrees as depicted in figures 1 and 2. In agreement with purely intuitive arguments, it was determined that the *cis* to *trans* barrier height is nearly 5.7–6.3 kcal mol<sup>-1</sup>. We next investigated the stability (relative to dissociation) for various regions of HSNO (shown in table 3) for the processes of atomization (1), S–N bond cleavage (2), and hydrogen abstraction (3) that may occur in the atmosphere.



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**Figure 1.** *Cis* and *trans* conformers of thionitrous acid (HSNO) and transition state for conversion of *cis* to *trans* conformer. TS ( $\tau = 86.9, 86.3,$  and  $87.7$  degrees at G2, CBS-Q, and CBS-QB3, respectively).

Table 3 shows the relative energies ( $\Delta E$ ) for different pathways. It can be seen in table 3 (it should be rather obvious) that *trans* decomposition energies are higher than all other pathways. The  $\Delta E_1$ : HSNO ( $\tau$ ) $\rightarrow$ H+S+N+O, pathways passes the highest energies of reaction, thus emphasizing the stability of this species towards atomization (in atmosphere or veins, for example), and lowest energy pathway is  $\Delta E_2$ : HSNO ( $\tau$ ) $\rightarrow$ SH+NO that gives radical species as products. From our energy analysis, a homolytic cleavage of bond S–N mechanism should be the most likely dissociation pathway.

In order to obtain a deeper insight into the reasons behind the order of stability for various conformers in the present study system, as well as to obtain more information about the direction and magnitude of intramolecular charge-transfer (CT) interaction, NBO<sup>11–16</sup> analysis was performed for all points on the relaxed torsional potential energy surface (PES). A second-order perturbation theory (SOPT) analysis of the Kohn–Sham one-electron analogue of the Fock matrix within the NBO basis was carried out for selected geometries obtained with partial geometry optimization for a fixed torsional angle.

**Table 1.** Computed total energies (in Hartrees) for species in decomposition of HSNO.

Species	G2	CBS-Q	CBS-QB3
H	−0.498584	−0.498402	−0.498402
S	−397.653524	−397.655471	−397.655956
N	−54.516543	−54.518827	−54.519121
O	−74.980614	−74.985643	−74.986213
SH	−398.284611	−398.287447	−398.288300
NO	−129.737606	−129.744709	−129.746108
SNO	−527.434934	−527.464615	−527.453917

Within the NBO approach, the estimated energetic effects due to CT interactions are given by the SOFT expressions from ref. 11:

$$\Delta E^{(2)}\psi_{\text{don}} \rightarrow \psi_{\text{acc}} \approx 2 \left( \frac{\langle \psi * | \hat{F} | \psi \rangle}{\varepsilon_{\text{acc}} - \varepsilon_{\text{don}}} \right)^2, \quad (1)$$

where  $\varepsilon_i$  is a diagonal NBO matrix element of the Fock operator  $F$ . The result from the SOPT analyses for all the considered structures are summarized in table 4. Only the most relevant CT contributions (in an energetic sense) and their variations with the change in torsional angle  $\tau$  are listed. It can be seen in table 4, that the CT from the LP(O) orbital to the S–N antibonding orbital (LP(O) $\rightarrow$ BD\*S–N) state, is energetically the most significant contribution to the overall system stability when CT interaction is in question. It also shows most pronounced torsional angle dependence, the corresponding  $\Delta E^{(2)}$  value increasing from 0 to 90°, and significantly decreasing as the angle  $\tau$  increases

**Table 2.** Computed relative total energies (in kilocalories per mole) for varying HSNO dihedral angle ( $\tau$ ) in degrees (°).

$\tau$ (°)	G2	CBS-Q	CBS-QB3
0	1.030	1.003	0.981
20	1.986	2.090	2.011
40	3.902	4.124	4.441
60	6.495	6.811	6.265
80	8.000	8.324	7.620
100	7.785	8.133	7.413
120	5.838	6.180	5.622
140	3.515	3.749	3.506
160	1.005	1.046	1.015
180	0	0	0

**Table 3.** Relative energy ( $\Delta E$ ) of the dissociation energy pathways (kcal mol<sup>-1</sup>) for  $\Delta E_1$ : HSNO ( $\tau$ ) $\rightarrow$ H+S+N+O,  $\Delta E_2$ : HSNO ( $\tau$ ) $\rightarrow$ HS+NO and  $\Delta E_3$ : HSNO ( $\tau$ ) $\rightarrow$ H+SNO.

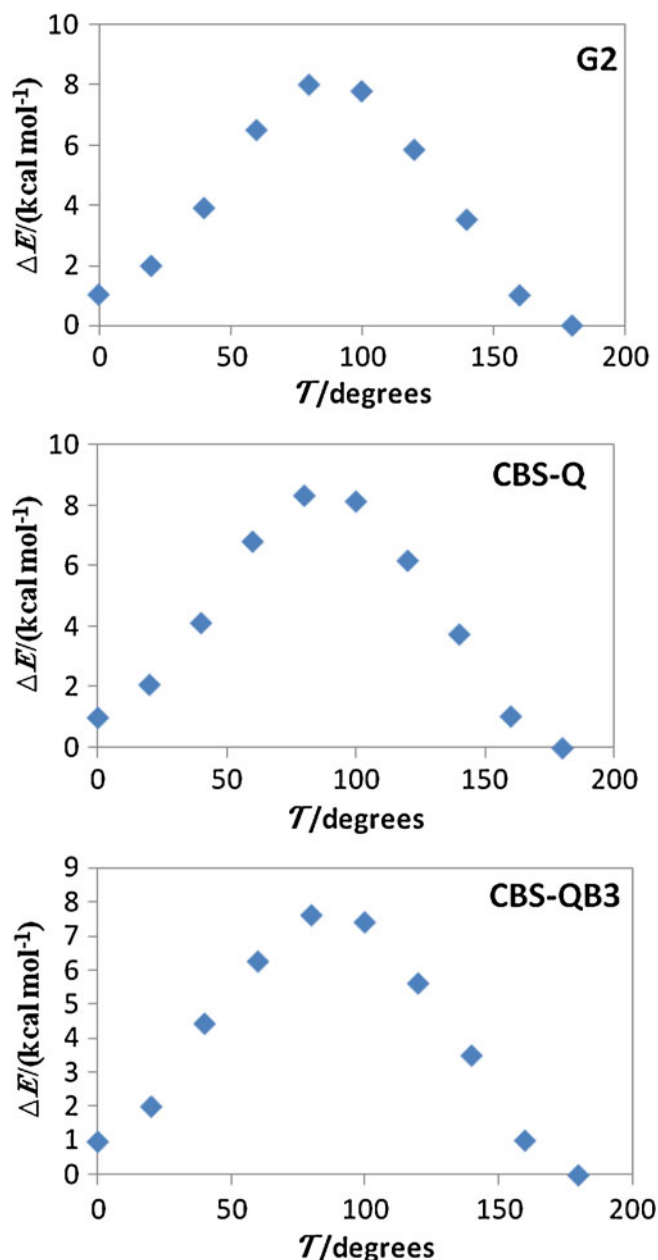
$\tau$ (°)	G2	CBS-Q	CBS-QB3
$\Delta E_1$			
0	262.863	263.750	263.302
20	261.801	262.663	262.272
40	259.991	260.629	259.843
60	257.398	257.942	258.019
80	255.893	256.430	256.662
100	256.109	256.620	256.870
120	258.056	258.573	258.662
140	260.385	261.004	260.778
160	262.889	263.707	263.269
180	263.893	264.753	264.283
$\Delta E_2$			
0	28.836	29.182	28.168
20	27.773	28.096	27.138
40	25.963	26.061	24.708
60	23.370	23.374	22.885
80	21.865	21.861	21.528
100	22.081	22.052	21.736
120	24.028	24.006	23.527
140	26.351	26.436	25.643
160	28.861	29.139	28.133
180	29.865	30.185	29.149
$\Delta E_3$			
0	84.495	72.567	79.679
20	83.432	71.480	78.649
40	81.622	69.446	76.219
60	79.029	66.759	74.396
80	77.523	65.246	73.039
100	77.740	65.437	73.247
120	79.687	67.390	75.038
140	82.010	69.821	77.154
160	84.520	72.524	79.645
180	85.524	73.570	80.660

to 180° for the most intramolecular CT contribution as shown in figure 3(a). Other significant contributions to the overall intramolecular CT are LP(S) $\rightarrow$ BD\*N-O, BD S-H $\rightarrow$ BD\*S-N, BD S-H $\rightarrow$ BD\*N-O, and BD S-N $\rightarrow$ BD\*NO.

Finally, the energy barriers calculated using the distinct theoretical approaches mentioned above were fitted to a potential function, represented by nine term truncated Fourier series,<sup>17</sup> as described in (2).

$$V(\tau) = \sum_{i=1}^9 (V_i/2) (1 - \cos(i\tau)), \quad (2)$$

where  $\tau$  is the torsional angle which is allowed to vary from 0 to 180° in steps of 20 degrees. It should be mentioned that in (2),  $V(\tau)$  is the relative energy at the rotational angle  $\tau$ , which has to be defined as (180° -  $\tau$ ) since *trans* was selected as the energy origin. The



**Figure 2.** Relative energies of HSNO molecule versus torsional angle at three computational levels.

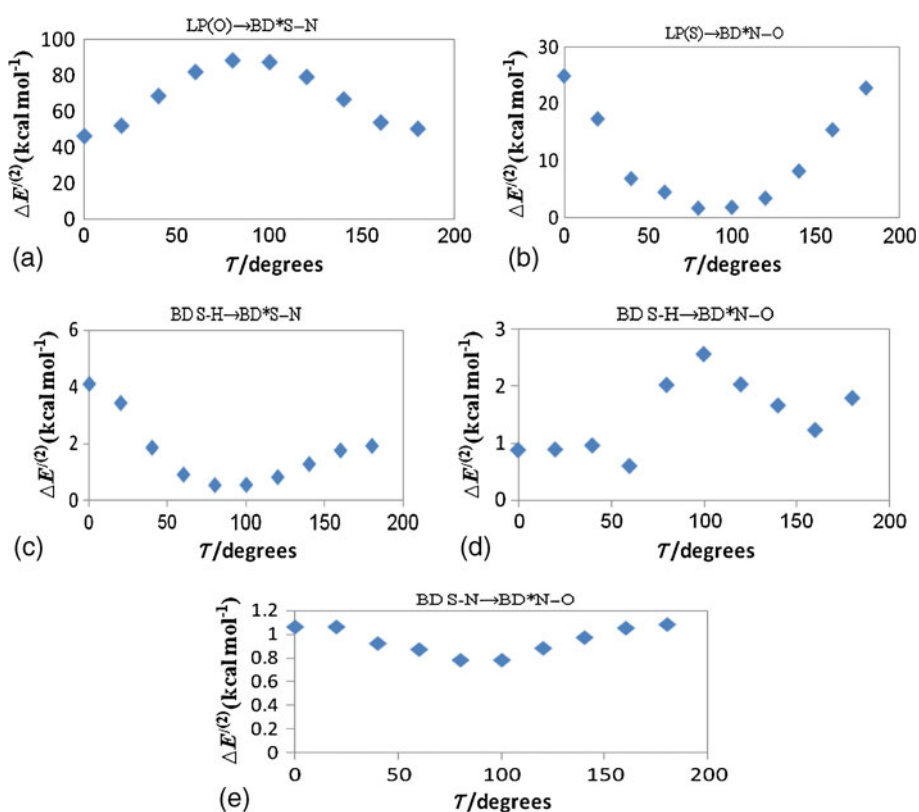
potential parameters obtained from the fitting are shown in table 5.

#### 4. Conclusions

In this study, we have presented the results of our G2, CBS-Q and CBS-QB3 calculations on the torsional dissociation and rotation barrier of HSNO. Our methods are generally in good agreement with one another regardless of the choice of optimization method for the first steps of the Gaussian calculations. It is interesting to note that the HSNO torsional potential correlated

**Table 4.** Result of the second-order perturbation theory (SOPT) analysis of the Kohn–Sham one analogue of the Fock matrix within the NBO basis for selected geometries obtained with partial geometry optimization for a fixed torsional angle.

$\tau$ (°)		0	20	40	60	80	100	120	140	160	180
Donor	Acceptor										
LP(O)	BD*S-N	46.43	52.18	68.67	82.02	88.38	87.37	79.23	66.81	53.98	50.46
LP(S)	BD*N-O	25.00	17.42	6.87	4.48	1.63	1.81	3.41	8.19	15.49	22.88
BD S-H	BD*S-N	4.10	3.43	1.86	0.91	0.54	0.55	0.82	1.28	1.76	1.92
BD S-H	BD*N-O	0.88	0.89	0.96	0.60	2.02	2.56	2.03	1.66	1.23	1.79
BD SN	BD*NO	1.06	1.06	0.92	0.87	0.78	0.78	0.88	0.97	1.05	1.08

**Figure 3.** Variation of energy of charge transfer energies with the torsional angle: (a) (LP(O)→BD\*S-N), (b) (LP(S)→BD\*N-O), (c) (BD S-H→BD\*S-N), (d) (BD S-H→BD\*N-O), and (e) (BD S-N→BD\*NO).**Table 5.** Result of a fit of the data in table 3 (relative energy) to the Fourier series as  $V(\tau) = \sum_{i=1}^9 (V_i/2) (1 - \cos(i\tau))$ .

	$v_1$	$v_2$	$v_3$	$v_4$	$v_5$	$v_6$	$v_7$	$v_8$	$v_9$
G2	0.932	7.513	0.021	0.004	0.210	0.110	-0.019	0.017	-0.115
CBS-Q	0.941	7.861	0.048	0.107	0.190	0.106	-0.043	0.023	-0.135
CVS-QB3	1.111	7.058	-0.100	0.390	-0.035	0.278	0.007	-0.178	-0.001

very well with a potential function, represented by nine terms truncated Fourier series.

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