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Theoretical Conformational Analysis of a Simple Sulphilimine Model

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The topomerization (bond rotation and *S*-pyramidal inversion) of a simple sulphilimine model, H_2SNH has been studied with the aid of *ab initio* SCF MO calculations. The highest rotation barrier occurs when the H_2SN moiety is planar, $< HSN = 120°$. The maxima of the inversion crossections occur at the planar conformation for all rotation angles α as expected, however, the minima belong to different values when α is varied. The minimum energy path between the two lowest minima of the conformational energy surface consists of a pure inversion section and a section which is mostly rotation. The optimum values of the $< HSN$ bond angles are significantly smaller than the corresponding $< RSN$ bond angles of sulphilimines of bulkier *R* substituents.

Key word: Sulphilimines

1. Introduction

In recent years the conformational behaviour of sulphilimines ($R, R'S = NQ$), containing a tri-coordinated sulphur atom and a sulphur-nitrogen bond, was investigated by various methods [1–5]. The central question was, whether the rather strong S–N bond, formally denoted as a double bond, has some characteristics resembling the $C=C$ double bond responsible for rigid molecular structures, or these molecules rather possess more conformational freedom.

X-ray investigations [1, 2] indicated that the S, S-dimethyl-N-methylsulphonyl sulphilimine (Me_2SNSO_2Me), possessing no chiral centre, exists in two asymmetric conformations in the crystalline state, with these conformations related to each other as enantiomers. However, no resolution of these enantiomers was successful [3], and it was believed that rotations about the SN and NS′ bonds can bring about the interconversion of the two forms. Previous semiempirical MO calculations [4, 5] supported this hypothesis, as the calculated barrier of interconversion *via* consecutive rotations was only 5.6 Kcal/mol.

The X-ray analysis revealed, however, that the thermal motion of the two neighbouring methyl groups is very intensive and has a fairly large component along the S-pyramidal inversion coordinate [1]. This result suggested that the pyramidal inversion on S, or a partial distorsion along this coordinate, could contribute to the conformational changes of these molecules.

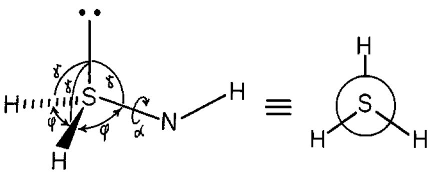
The above experimental findings and theoretical results motivated our present *ab initio* study on the interaction of rotation and inversion in sulphilimines. The previous semiempirical calculations suggested that the conformational behaviour of sulphilimines was strongly dependent on the size of different substituents R, R′, Q. In order to minimize the effect of substituents the H_2SNH parent compound of sulphilimines was chosen as model for our investigations.

The calculations were carried out on an IBM 370/165 computer, using a version of the Gaussian 70 program [6].

2. Results and Discussion

In all the *ab initio* calculations performed for the model compound H_2SNH the S–N bond length was taken to be equal to 1.53 Å to simulate a S–N double bond. The S–H and N–H bond lengths were taken as 1.33 Å and 1.04 Å, respectively. The SNH bond angle was chosen to be 120°. The S–N bond rotation coordinate α took values from 0° to 180°, $\alpha = 0°$ corresponding to the "Y" conformation shown in Fig. 1. The pyramidal inversion coordinate γ, as defined in Fig. 1, took values from 50° to 130°. A split valence shell basis set (4-31 G) was used throughout the present study, these AO bases are defined in Refs. [7] and [8].

The rotation-inversion scheme is shown in Fig. 2. The calculated total energy as a function of the rotation angle α and inversion angle γ was evaluated at a



$$\varphi = \cos^{-1}\left\{\frac{1}{2}\left[3\sin^2(\gamma-90)-1\right]\right\}$$

Fig. 1. Definition of topomerization coordinates for sulphilimine model H_2SNH

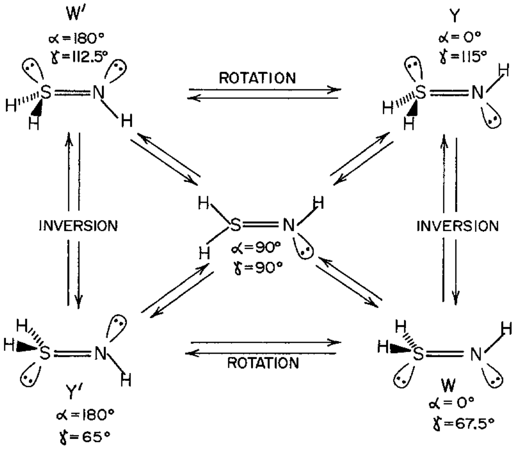


Fig. 2. Topomerization scheme for H_2SNH

Table 1. Relative energy values[a] of the conformational energy surface of HN–SH_2

γ/α	0(180)	45(135)	90	135(45)	180(0)
90.0	24.44	34.25	45.46	34.25	24.44
95.0 (85.0)	23.83	32.65	41.46	29.69	20.70
100.0 (80.0)	18.31	25.45	30.35	21.42	12.91
105.0 (75.0)	10.31	15.93	20.99	13.08	6.03
109.5 (70.5)	3.79	8.47	13.39	8.08	2.42
115.0 (65.0)	0.00	4.01	9.60	7.74	3.82
120.0 (60.0)	2.92	6.57	13.23	14.78	12.54
130.0 (50.0)	34.42	36.44	45.63	55.07	56.89

[a] Values are relative to the most stable conformational corresponding to $\alpha = 0°$, $\gamma = 115°$ or, $\alpha = 180°$, $\gamma = 65°$.
All Values are given in Kcal/mol units.

total of 40 points, and a topomerization energy surface was generated. The calculated energy values are listed in Table 1, while the rotation-inversion energy surface is shown in Fig. 3.

The energy surface has four minima. The two lowest minima, corresponding to the two equivalent conformations Y and Y′, occur at $\alpha = 0°$, $\gamma = 115°$ and $\alpha = 180°$, $\gamma = 65°$, respectively. The calculated total energy at these points is equal to −452.948133 hartree and is chosen as 0.0 Kcal/mol on the relative scale. The two other minima, corresponding to equivalent conformations W and W′ occur at $\alpha = 0°$, $\gamma = 70.5°$ and $\alpha = 180°$, $\gamma = 109.5°$, respectively. The total energy of conformers W and W′ is 2.42 Kcal/mol on the relative scale.

The highest energy maximum of the surface occurs at $\alpha = \gamma = 90°$, which corresponds to the planar conformation.

The lowest energy paths between the two minimum points Y and Y′, *via* Y–W–Y′, and Y–W′–Y′ consist of two types of conformational changes. The changes along sections Y–W and W′–Y′ are pure inversions, along sections Y–W′ and W–Y′ the rotation dominant change is accompanied by a slight change of 5.5° along the inversion coordinate. The significant energy values belonging to various crossections of the energy surface are presented in Table 2.

The highest energy barrier along the minimum energy path occurs in the pure inversion section and equals to 24.44 Kcal/mol. This result indicates that in

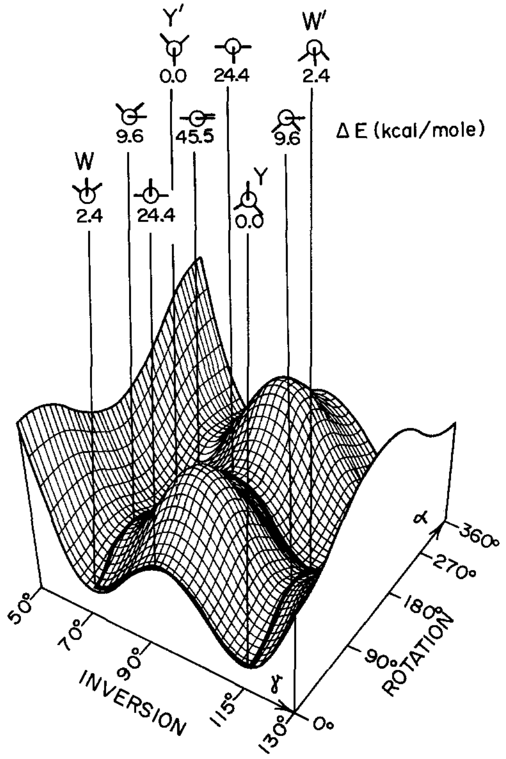


Fig. 3. Conformational energy surface for H_2SNH. (Relative energies in Kcal/mol as measured from conformation $\alpha = 0°$, $\gamma = 115°$)

Table 2. Energy barriers of various crossections of the energy surface

Crossection	Barrier [Kcal/mol]
Rotation (α) at $\gamma = 115°$ or $\gamma = 65°$	9.60
Inversion (γ) at $\alpha = 0°$ or $\alpha = 180°$	24.44
Simultaneous rotation and inversion	45.46

simple sulphilimines the Y–Y′ type conformational change is inversion dominant. The path along the diagonal of the total energy surface, that involves simultaneous rotation and inversion, goes through the highest maximum of 45.46 Kcal/mol.

3. Conclusions

The results of the present model study on the interaction of rotation and pyramidal inversion of the H_2SNH molecule suggest that the pyramidal inversion has only a minor contribution to the most frequent conformational changes of actual sulphilimines. The calculated inversion barrier of the H_2SNH molecule is

24.44 kcal/mol. It is remarkable, that the optimum H–S–N bond angle is much smaller than the corresponding experimental R–S–N bond angle in sulphilimines with larger R groups.

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