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Ab Initio Calculations of the Rotational Barrier in Dimethyl Diselenide

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ABSTRACT

The heights of the rotational barriers of the diselenide bridge in dimethyl diselenide have been calculated at the Hartree-Fock level with the 3-21G basis set. The minimum in the rotational potential energy function occurs at a torsional angle of 85.64°. The barriers were determined by complete geometry optimization at each point along the potential surface. The results are compared with other calculations and with the available experimental results. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The experimental effort in our laboratory is directed toward the understanding of the chemistry involved in optical methods of chemical vapor deposition. Recently we have explored the photochemistry of a number of organoselenium molecules [1]. As part of our attempt to understand this chemistry, we have turned to the use of computational methods to assist in sifting through photochemical kinetic pathways. Increasingly, the nature of rotational barriers in these molecules, while not a part of the kinetic studies, has attracted our attention for the fundamental information it provides. We have recently reported on the rotational barriers in a series of benzeneselenenyl molecules and cations [2,3].

The dimethyl diselenide molecule has been an important part of our kinetic studies, especially as a comparison point with the mono-selenium compound. The diselenide is also of interest computationally as an analog to the peroxide and disulfide molecules that are more prevalent in chemistry. As was noted in an earlier computational study, dimethyl diselenide is the simplest organoselenium molecule containing the diselenide bridge. The rotational barrier for this molecule is then interesting as a model for the same process in more complex molecules, such as those containing cystine [4].

We report here on a study to determine the potential function for rotation about the diselenide bridge. The molecular geometry was fully optimized at all points along this surface. The results indicate that the barrier is significantly greater for the *cis* orientation than for the *trans* form, in agreement with experimental observations.

CALCULATIONS

Previous studies have indicated that the use of electron correlation with the basis sets available for selenium leads to poorer agreement with the experimental data [2,3]. The results reported here have been restricted to the Hartree-Fock level only. Among the widely used basis sets, the available basis sets for selenium include STO-3G and 3-21G, as well as the LANL1DZ basis set which combines the STO-3G functions for first row atoms with an effective core potential basis set for selenium. Our experience, as well as that of other researchers, indicates that the 3-21G basis set provides the best computational performance. The reported calculations employ the GAUSSIAN 92 [5] suite of programs. No constraints were imposed during geometry optimization to locate the global minimum. At other points along the potential energy surface, the geometries were fully optimized with the exception of the torsional angle, which was set to a selected value. The geometries and energies represent fully relaxed points along the

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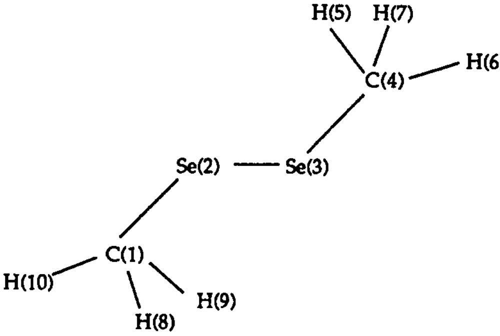
TABLE 1 Optimized Geometric Parameters for Dimethyl Diselenide as a Function of the Torsional Angle



	Torsional Angle (°)								
Parameter	0	20	45	70	85.6	110	135	160	180
Se–Se	2.522	2.513	2.486	2.465	2.463	2.471	2.488	2.500	2.502
C–Se	1.980	1.979	1.980	1.981	1.982	1.983	1.983	1.982	1.981
C–H_5	1.077	1.077	1.077	1.078	1.078	1.078	1.078	1.078	1.078
C–H_6	1.082	1.082	1.081	1.081	1.081	1.081	1.081	1.081	1.081
C–H_7	1.077	1.078	1.078	1.078	1.077	1.077	1.078	1.078	1.078
<Se–Se–C	101.62	101.07	99.72	98.90	98.87	98.49	97.16	95.86	95.46
<H_5–C_4–Se_3	110.93	110.75	110.40	110.30	110.26	110.16	109.96	109.96	110.05
<H_6–C_4–Se_3	105.18	105.41	106.12	106.57	106.58	106.44	106.40	106.40	106.44
<H_7–C_4–Se_3	110.93	110.85	110.30	109.90	109.79	109.86	110.00	110.12	110.05
<H_5–C_4–Se_3–Se_2	−62.06	−63.14	−67.54	−65.04	−64.17	−61.29	−58.40	−59.29	−61.19
<H_6–C_4–Se_3–Se_2	179.91	178.76	174.01	176.21	176.84	179.54	182.47	181.78	180.02
<H_7–C_4–Se_3–Se_2	61.88	60.56	55.40	7.23	57.90	60.77	563.79	63.09	61.23
Rel. energy, au[a]	−0.75050	−0.75224	−0.75715	−0.76102	−0.76169	−0.76048	−0.75793	−0.75584	−0.75527

[a] Defined relative to an absolute energy of −4855.00000 hartree.

TABLE 2 Calculated Barrier Heights in kcal mol^{-1} for $(CH_3)_2Se_2$ and $(CH_3)_2S_2$

Molecule[a]	*Isomer*	*Optimal Geometry*[b]	*Fixed Geometry*[c]
CH_3–Se–Se–CH_3	*cis*	7.02	8.56
	trans	4.03	4.83
CH_3–S–S–CH_3	*cis*	7.42	11.15
	trans	2.89	3.48
CH_3–S–S–CH_3 (6-31G*)	*cis*	11.05	
	trans	5.38	

[a] HF/3-21G unless noted otherwise.
[b] Fully optimized geometry (fixed torsional angle).
[c] Geometry fixed to fully optimized values (except for torsional angle).

potential surface. Frequency calculations were obtained to identify the optimized geometries as saddle points or as a minimum on the potential surface. Molecular orbitals were examined using the natural bond orbital approach.

RESULTS AND DISCUSSION

Table 1 shows the results of the geometry optimizations. A pictorial view of the optimized geometry, as well as the *cis* and *trans* geometries, is presented in Figure 1. The equilibrium value for the torsional angle was determined to be nearly perpendicular, 85.64°. For the fully optimized geometry, the Se atom, as expected from general considerations, appears to have far more p character than oxygen or sulfur; the Se–Se–C bond angle is ~99° for the equilibrium structure and acquires additional p character as the angle approaches the *trans* configuration. However, the Se atom becomes more tetrahedrallike as the geometry is varied toward the *cis* configuration. The only previous ab initio calculations [4] did not involve full optimization of all of the coordinates, so this effect has not been previously reported. Moreover, the earlier study involved variation of the torsional angle by an arbitrary amount and could only estimate the equilibrium value to be ~90° from a least squares fit to the limited data [4]. The conformation has also been reported from electron diffraction studies [6]. The experimental Se–Se and Se–C bond distances were observed to be 2.326 and 1.954 Å, respectively, and the Se–Se–C and torsional angles were reported to be 98.9 and 87.5°. The present calculation overestimates the bondlengths by 6

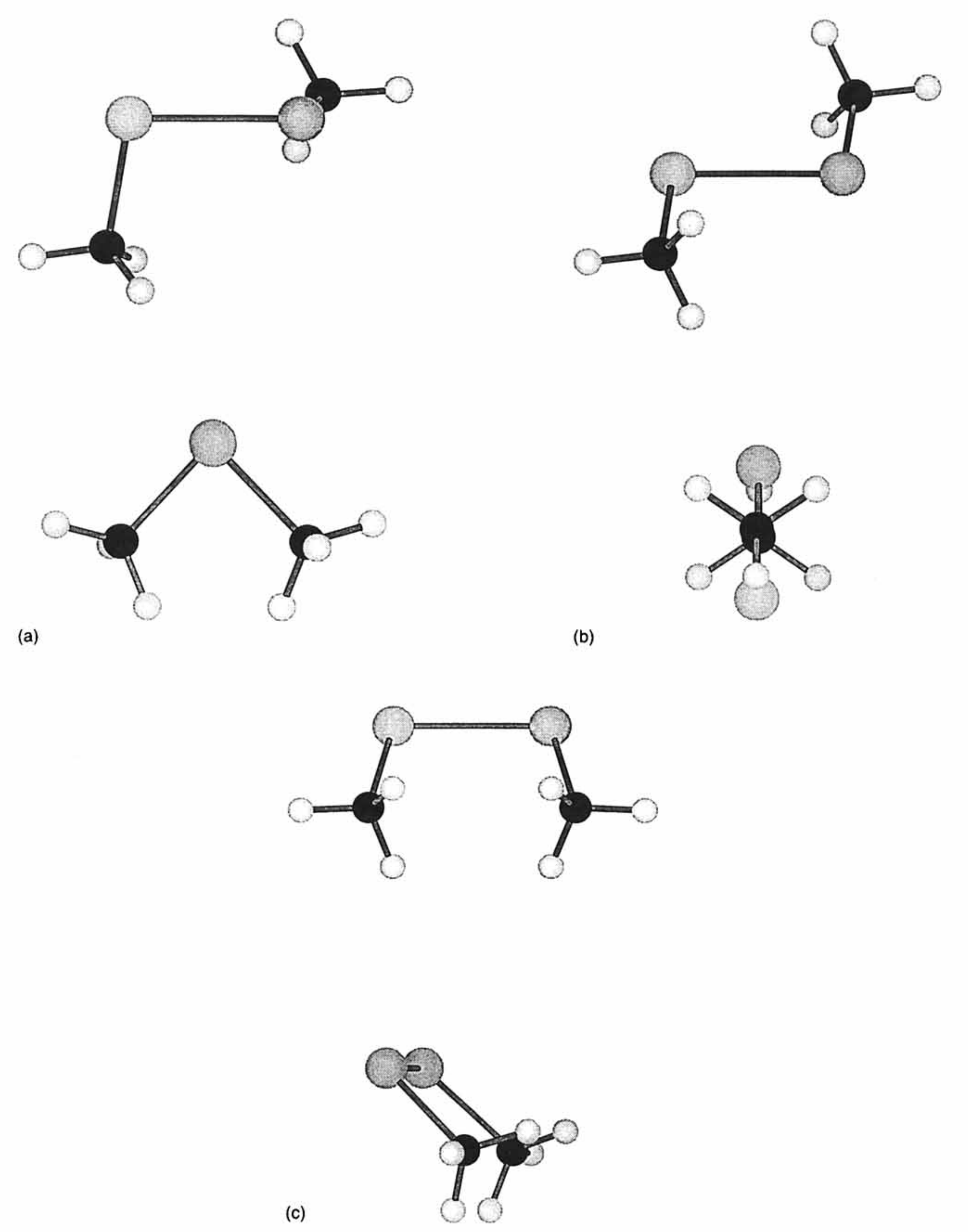


FIGURE 1 (a) Fully optimized (HF/3-21G) geometry for dimethyl diselenide; (b) the fully optimized *trans* configuration and (c) the fully optimized *cis* configuration. Views along two different axes are provided for each geometry.

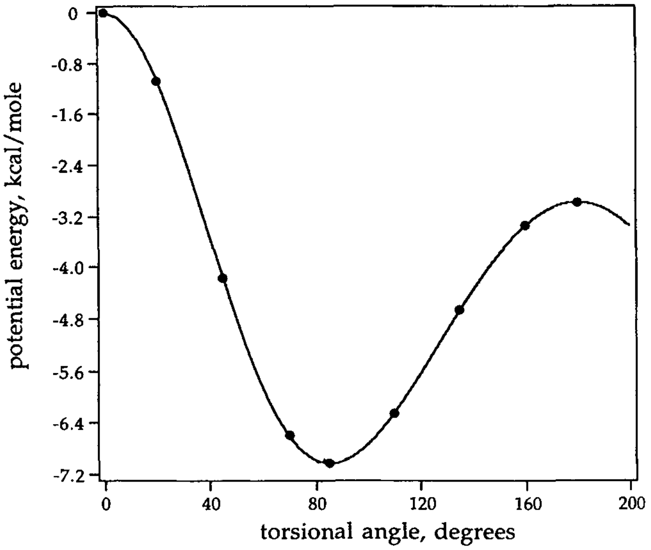


FIGURE 2 Dimethyl diselenide rotational potential energy function. Details of the fitting function are provided in the text.

and 1.5%, respectively, but exhibits better agreement for the bond angles. The lack of agreement may be a result of the fact that the experimental value is averaged over all possible configurations, while the calculated value is the true equilibrium geometry. Given the level of the basis set, the agreement is regarded as very good.

Absolute energies are also contained in Table 1. The torsional energy is plotted as a function of angle in Figure 2 and the calculated barrier heights are presented in Table 2. The *cis* barrier is significantly greater than the *trans* barrier. For comparison, the *cis* and *trans* barriers for dimethyl disulfide have been calculated, at the same level of theory, with full optimization. Table 2 indicates that the Se and S *cis* barriers are comparable, but that the *trans* barrier for the sulfur analog is only about 75% of that for the Se molecule. In order to test the effect of basis set size, the barriers in dimethyl disulfide were also computed using the 6-31G* basis set with full optimization. The barriers to both the *cis* and *trans* configurations increase significantly. We interpret this as an indication that the 3-21G basis set may be underestimating the actual barrier heights. Nevertheless, since equivalent HF/3-21G calculations were performed for both selenium and sulfur analogs, the calculations indicate that barriers to *cis* rotation are comparable for dimethyl selenide and dimethyl sulfide, while the barrier to *trans* rotation is approximately 25% greater for the selenium molecule. Also included in Table 2 is a comparison of the predicted barrier heights from a calculation in which the molecule is fixed in the optimized geometry and only the torsional angle is varied. This latter approach was taken in an earlier computational study [4]. It may be observed that the barrier heights are significantly overestimated by this approximate calculation.

The rotational potential energy may be expanded as a series of the form

$$V(\Theta) = V_1(1 - \cos\Theta) + V_2(1 - \cos 2\Theta) + V_3(1 - \cos 3\Theta) + V_4(1 - \cos 4\Theta) \quad (1)$$

where Θ is the C–Se–Se–C torsional angle. The data set consists of nine fully optimized geometries and the resulting fit to Equation 1 is

$$V(\Theta) = -0.92(1 - \cos\Theta) - 2.75(1 - \cos 2\Theta) - 0.57(1 - \cos 3\Theta) - 0.09(1 - \cos 4\Theta) \quad (2)$$

The origin of a rotational barrier such as that described for dimethyl diselenide has not been completely assigned. Some of the suggested origins, within the context of Hartree-Fock theory, have been summarized in the review by Veillard [7]. The postulated origins include changes in the various terms (V_{nn}, V_{ne}, T, and V_{ee}) that contribute to the total molecular energy, as well as decompositions of these terms into attractive and/or repulsive components [8–10]; however, many of these decompositions produce different results depending upon the basis set and others are untested for any but a few molecules. Other researchers have attempted to apply localized orbitals [11], electron density calculation [12], wave function analysis [13], or total overlap population analysis [14] to this barrier problem. These latter related methods, which are conceptually simple, appear to provide some physical insight into the nature of the rotational barrier, and we have chosen to explore their application to the current problem. Table

TABLE 3 Overlap Populations from the HF/3-21G Model

	Overlap Population						*Total Charge*				
	Se–Se	*C–Se*	*C_4–H_5*	*C_4–H_6*	*C_4–H_7*	*Overlap Charge*	*Se*	*C*	*H_4*	*H_5*	*H_6*
opt	0.344	0.316	0.720	0.702	0.720	4.441	0.153	−0.901	0.244	0.246	0.257
cis	0.276	0.350	0.716	0.712	0.716	4.481	0.157	−0.912	0.249	0.256	0.249
trans	0.274	0.354	0.716	0.712	0.716	4.479	0.149	−0.912	0.255	0.252	0.252

3 provides overlap populations, atomic charges, and total overlap populations for the three geometries shown in Figure 1. Both transition state geometries involve reduction of the overlap population between the two selenium atoms. In addition, the *cis* configuration also requires that the charge on the hydrogens in this eclipsed geometry, in comparison with the *trans* configuration, be significantly reduced. These results are consistent with those reported for the related hydrogen peroxide molecule [15], in which the barriers are attributed to a reduction in the overlap population of the O–O bond, as well as interaction of the hydrogens in the *cis* configuration. The total overlap population analysis is also consistent with the observations. The optimized geometry represents the state with the greatest overlap population and the order of the relative stabilities follows the order of increasing total overlap population, with the caveat that the difference in overlap charges for the two transition state geometries is not large.

In summary, we have used ab initio calculations to determine the rotational barriers in the simple dichalgogenide, dimethyl diselenide, using fully optimized geometries. The results indicate that the *cis* barrier is comparable to that obtained by the same calculation for the disulfide analog, but that the *trans* barrier is significantly larger. The structural results are consistent with the available experimental data.

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