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# Ab Initio Calculations of the Rotational Barriers in $H_2Te_2$ and $(CH_3)_2Te_2$

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## ABSTRACT

*The heights of the rotational barriers of the ditelluride bridge in* $H_2Te_2$ *and* $(CH_3)_2Te_2$ *have been calculated at the Hartree–Fock level with the 3-21G basis set. The minima in the rotational potential energy functions occur at torsional angles of 87.58° and 89.32°, respectively. The barriers were determined by complete geometry optimization at each point along the potential surface. In addition, preliminary results on the stability of* $H_2Te_2$ *are reported. The molecule is found to be stable with respect to dissociation into* $H_2Te$ + Te *or* $H_2$ + $Te_2$. *© 1997 John Wiley & Sons, Inc. Heteroatom Chem* **8**: *199–202, 1997.*

## INTRODUCTION

The experimental effort in our laboratory is directed toward the understanding of the chemistry involved in optical methods of chemical vapor deposition [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 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 and for dimethyl diselenide in comparison to dimethyl disulfide [2,3].

The $H_2Te_2$ and $(CH_3)_2Te_2$ molecules have not been involved in many experimental studies. Indeed, the question of the stability of $H_2Te_2$ in relationship to its possible dissociation products, $H_2Te$ + Te and $H_2$ + $Te_2$, is still a matter of controversy. The ditellurides are of interest computationally as analogs to the previously reported calculations involving the more commonly encountered molecules from group 16.

We report here on a study to determine the potential function for rotation about the ditelluride bridge in both molecules. 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 addition, we have explored the relative stability of $H_2Te_2$ and find that, in agreement with the mass spectral results recently reported, the molecule is indeed stable with respect to dissociation into either set of potential products.

## 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]; therefore, we have restricted our calculations to Hartree–Fock methods for Te as well. Among the widely used basis sets, those available for tellurium include STO-3G and 3-21G, as well as the LANL1DZ basis set that combines the STO-3G functions for first-row atoms with an effective core potential for tellurium. Our experience, as well as that of other researchers, indicates that the 3-21G basis set provides the best computational performance from among these choices. The reported calculations employ the GAUSSIAN 92 [4] suite of pro-

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grams. 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 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*

We have previously shown that a calculation in which the molecule is fixed in the optimized geometry and only the torsional angle is varied leads to barrier heights that are significantly overestimated. Tables 1 and 2 show the results of the full geometry optimizations. The tables only present those structural parameters that vary with the torsional angle. A pictorial view of the optimized geometry, as well as the *cis* and *trans* geometries, is presented in Figures 1 and 2. All parameters are included in the figures for the geometries shown.

*The Stability of $H_2Te_2$.* The stability of this molecule has been a matter of controversy. The most recent experimental evidence, obtained indirectly via mass spectral measurements [5], indicates that the molecule is stable with respect to dissociation. Two dissociation channels are possible:

$$H_2Te_2 \rightarrow H_2Te + Te \tag{1}$$

**TABLE 1** Energies and Structural Parameters[a] for $H_2Te_2$

| *Torsional Angle* | $d_{Te\text{–}Te}$ | *<Te–Te–H* | *Energy, kcal/mole* |
|---|---|---|---|
| 0.0 | 2.934 | 92.79 | 0.00 |
| 10.0 | 2.932 | 92.86 | −0.15 |
| 25.0 | 2.922 | 93.22 | −0.89 |
| 40.0 | 2.907 | 93.77 | −2.02 |
| 55.0 | 2.893 | 94.46 | −3.23 |
| 70.0 | 2.883 | 94.91 | −4.19 |
| 89.32 | 2.879 | 94.93 | −4.69 |
| 105.0 | 2.882 | 94.47 | −4.38 |
| 120.0 | 2.892 | 93.67 | −3.63 |
| 135.0 | 2.904 | 92.74 | −2.68 |
| 150.0 | 2.915 | 91.87 | −1.80 |
| 165.0 | 2.922 | 91.25 | −1.19 |
| 180.0 | 2.925 | 91.03 | −0.98 |

[a] Distances in Å, angles in degrees, and energy relative to torsional angle of 0°. Structural parameters not shown remain essentially invariant with changes in torsional angle.

**TABLE 2** Energies and Structural Parameters[a] for $(CH_3)_2Te_2$

| *Torsional Angle* | $d_{Te\text{–}Te}$ | *<Te–Te–C* | *Energy, kcal/mole* |
|---|---|---|---|
| 0.0 | 2.933 | 97.92 | 0.00 |
| 10.0 | 2.930 | 97.79 | −0.25 |
| 25.0 | 2.917 | 97.24 | −1.37 |
| 40.0 | 2.898 | 96.71 | −2.93 |
| 55.0 | 2.880 | 96.61 | −4.39 |
| 70.0 | 2.867 | 97.04 | −5.39 |
| 87.58 | 2.866 | 97.42 | −5.80 |
| 105.0 | 2.869 | 97.19 | −5.43 |
| 120.0 | 2.882 | 96.42 | −4.64 |
| 135.0 | 2.893 | 95.49 | −3.64 |
| 150.0 | 2.903 | 94.60 | −2.69 |
| 165.0 | 2.910 | 93.97 | −2.02 |
| 180.0 | 2.913 | 93.75 | −1.78 |

[a] Distances in Å, angles in degrees, and energy relative to torsional angle of 0°. Structural parameters not shown remain essentially invariant with changes in torsional angle.

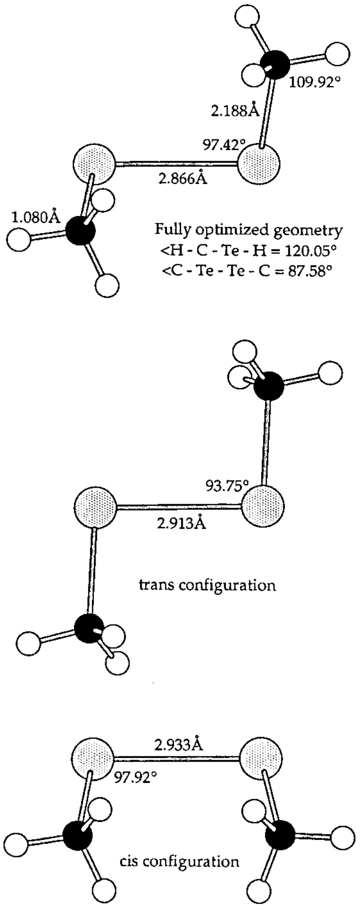

**FIGURE 1** Fully optimized (HF/3-21G) geometry for $(CH_3)_2Te_2$ as well as the fully optimized *trans* and *cis* configurations.

$$H_2Te_2 \rightarrow H_2 + Te_2 \qquad (2)$$

Ab initio estimates of the heats of reaction for these two processes yield values of ~1 kcal $mole^{-1}$ and ~ −1 kcal $mole^{-1}$, respectively. Since the basis set available for Te is relatively small, the exact value of the calculation is less important than the general conclusion that the reactions are essentially thermoneutral. Thermodynamically, there is little to choose from among the three possibilities of $H_2Te_2$, $H_2Te$ + Te, or $H_2$ + $Te_2$. Our expectation is, however, that it is kinetics that control the stability. In this sense, we need not the heat of reaction but the activation energy along the two potential energy surfaces. Once again, we are limited in the details that may be quantitatively extracted from the calculations reported here, but estimates of the energy of activation from complete optimization of the transition states leading from $H_2Te_2$ to the two products predict barriers of 44 and 73 kcal $mole^{-1}$, respectively, for reactions 1 and 2, with transition state geometries that are productlike in structure. One may conclude from this calculation that there is a barrier, that it is reasonably significant, and that the $H_2Te_2$ molecule would be expected to be observed experimentally before any dissociation occurs. This is in agreement with the reported experimental data [5].

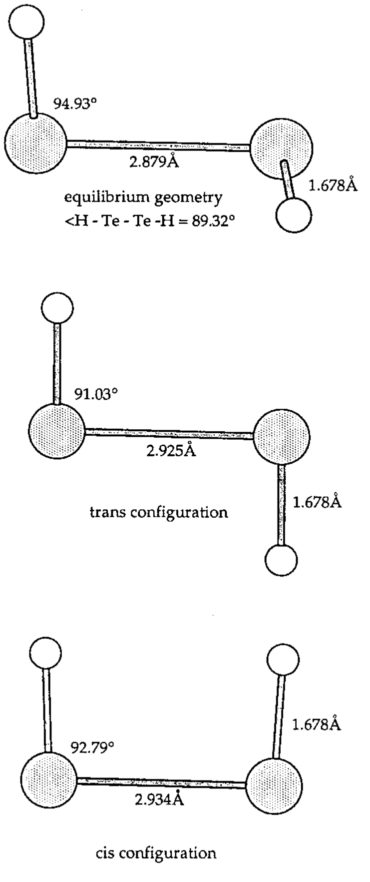

**FIGURE 2** Fully optimized (HF/3-21G) geometry for $H_2Te_2$ as well as the fully optimized *trans* and *cis* configurations.

*Rotational Barriers.* The equilibrium values for the torsional angle were determined to be nearly perpendicular, 89.32° for $(CH_3)_2Te_2$ and 87.58° for $H_2Te_2$. For the fully optimized geometry, the Te atom, as expected from consideration of our previous $(CH_3)_2Se_2$ results [2,3], appears to have far more *p* character than oxygen or sulfur. The Te–Te–C (or Te–Te–H) bond angle is ~97° (~94° for $H_2Te_2$) for the equilibrium structures and acquires some additional *p* character as the angle approaches the *trans* configuration. The only previous ab initio calculations [6,7] either did not involve full optimization of all of the coordinates or used a less sophisticated model, and they only report on the $H_2Te_2$ molecule. The parameters reported in the most recent and oft-cited study [7] include Te–Te and Te–H bond distances of 2.73 and 1.67 Å, respectively, and Te–Te–H and torsional angles of 72° and 76°. The agreement with the current results is rather poor. However, the computational method used here is superior to that in the earlier work, and the reported results are consistent with the Se results, which were shown to be in satisfactory agreement with experimental results. Energies relative to the *cis* configuration are also contained in Tables 1 and 2. The torsional energy is plotted as a function of angle in Figure 3. The *cis*

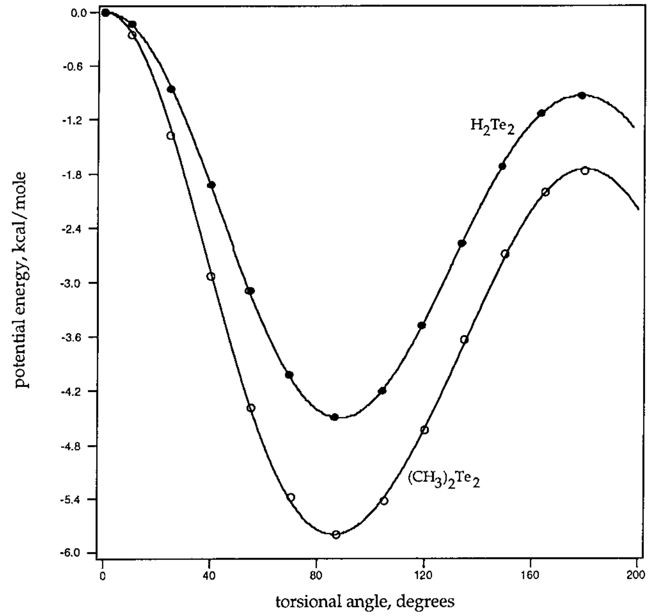

**FIGURE 3** Rotational potential energy functions for $H_2Te_2$ and $(CH_3)_2Te_2$. Details of the fitting function are provided in the text.

barrier [4.69 kcal mole$^{-1}$ for $H_2Te_2$ and 5.80 kcal mole$^{-1}$ for $(CH_3)_2Te_2$] is greater than the *trans* barrier (3.71 and 4.02 kcal mole$^{-1}$, respectively). $(CH_3)_2Te_2$ barriers are comparable to those obtained for dimethyl diselenide (7.08 and 4.30 kcal mole$^{-1}$ for the diselenide *cis* and *trans* barriers, respectively). The 3-21G basis set may be underestimating the actual barrier heights [3]. Nevertheless, since equivalent HF/3-21G calculations were performed for the selenium and sulfur analogs, the calculations indicate that barriers to *cis* rotation are identical for the selenium and tellurium molecules and approximately 40% larger than that for the sulfur analog. The barrier to *trans* rotation in the ditelluride continues the observed decrease down the periodic table.

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 $\Theta$ is the C–Te–Te–C or H–Te–Te–H torsional angle. The data set consists of nine fully optimized geometries, and the resulting fit to Equation 1 for $H_2Te_2$ is

$$V(\Theta) = -0.33(1 - \cos\Theta) - 2.10(1 - \cos 2\Theta) - 0.16(1 - \cos 3\Theta) - 0.02(1 - \cos 4\Theta) \quad (2)$$

while that for $(CH_3)_2Te_2$ is

$$V(\Theta) = -0.52(1 - \cos\Theta) - 2.45(1 - \cos 2\Theta) - 0.36(1 - \cos 3\Theta) - 0.01(1 - \cos 4\Theta) \quad (3)$$

The origin of the rotational barrier has not been completely assigned. We have previously applied the concepts of wave-function analysis [8] and total overlap population analysis [9] to this barrier problem. As was true in the case of the analogous Se compounds, both the *cis* and *trans* geometries involve reduction of the overlap population between the two tellurium atoms. In addition, the *cis* configuration also requires that the charge on the hydrogens in the eclipsed methyl groups or the hydrogens in $H_2Te_2$, in comparison with the *trans* configuration, be significantly reduced. These results are consistent with those reported for the related hydrogen peroxide molecule [10], 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 optimized geometry represents the state with the greatest overlap population, and the order of the relative stabilities from among the optimized, *cis* and *trans* geometries, follows the order of increasing total overlap population.

In summary, we have used ab initio calculations to determine the rotational barriers in two simple ditelluride molecules, using fully optimized geometries. The results indicate that the barriers for $(CH_3)_2Te_2$ are approximately 15% smaller than those of the corresponding diselenide. In addition, we have shown that the simplest ditelluride, $H_2Te_2$, is stable with respect to dissociation. This latter result is consistent with available experimental data.

## *ACKNOWLEDGMENTS*

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## *REFERENCES*

[1] J. J. BelBruno, J. Spacek, E. Christophy, *J. Phys. Chem., 95,* 1991, 6928; J. J. BelBruno, *ACS Symposium Series-Laser Chemistry of Organometallics,* p. 49 (1993).

[2] J. J. BelBruno, *J. Mol. Struct. (Theochem), 358,* 1995, 125.

[3] J. J. BelBruno, *Heteroatom Chem., 7,* 1996, 39.

[4] GAUSSIAN 92, Revision A, M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. DeFrees, J. Baker, J. J. P. Stewart, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 1992.

[5] C. E. A. C. Hop, M. A. Medina, *J. Am. Chem. Soc., 116,* 1994, 3163.

[6] C. S. Ewig, E. H. Mei, J. R. van Wazer, *Mol. Phys., 40,* 1980, 241.

[7] R. Block, L. Jansen, *J. Chem. Phys., 82,* 1985, 3322.

[8] W. L. Jorgensen, L. C. Allen, *J. Chem. Phys., 93,* 1971, 567.

[9] J. J. Kaufman, *Int. J. Quant. Chem., S1,* 1967, 485.

[10] A. Veillard, *Theoret. Chim. Acta, 18,* 1970, 21.