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# Far-Infrared and Raman Spectra of the Ring-Puckering Vibration of 2,3-Dihydrothiophene. One- and Two-Dimensional Potential Energy Surfaces and the Barrier to Planarity

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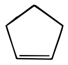
The vapor-phase far-infrared and Raman spectra of 2,3-dihydrothiophene have been recorded and analyzed. The infrared spectra show more than fifty transition frequencies corresponding to $\Delta v_P = 1, 2, 3, 4$, and 5 transitions. The ring-puckering energy levels were determined for both the ring-twisting ground and excited states. Both one- and two-dimensional potential energy functions, which fit the observed data very well, were determined. The barrier to planarity was determined to be 430 $cm^{-1}$ from the one-dimensional model and 435 $cm^{-1}$ for the two-dimensional model. The experimental dihedral angle of puckering is 31°, while an *ab initio* calculation predicts 29°. The magnitude of the interaction constant between the puckering and twisting was found to be $1.67 \times 10^5$ $cm^{-1}/Å^4$, similar to the values determined for related molecules.

## Introduction

Far-infrared and Raman spectra of cyclic and bicyclic molecules have been used since the 1960s to determine their ring-puckering potential energy functions.[1−5] Among these have been the "pseudo-four-membered rings" of the cyclopentene family where the C═C group is rigidly held together and thus vibrates as a single atom during the puckering motion. Some of the pseudo-four-membered-ring molecules are shown below. Cyclopentene[6] (**I**) itself is puckered due to the $-CH_2-CH_2-$ torsional interactions with a barrier to planarity of 232 $cm^{-1}$ and a dihedral angle of 26°. The other symmetric molecules (**II** to **VI**) are all planar as they lack these torsional interactions.[1−5] 1,3-Dioxole[7] (**VII**) is an exception as it has a barrier of 325 $cm^{-1}$ due to the anomeric effect.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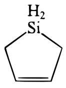

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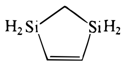

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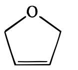

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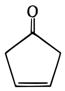

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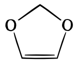

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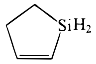

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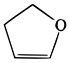

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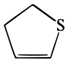
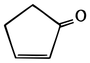


X



XI

Of the asymmetrically substituted molecules, XI is planar due to conjugation[8] as is **VIII** due to the interactions between the C═C double bond and the silicon atom.[9,10] 2,3-Dihydrofuran (**IX**) is nonplanar with a barrier of 83 $cm^{-1}$ based on far-infrared,[11] Raman,[12] and microwave[13] investigations. The ring-puckering potential function for 2,3-dihydrothiophene (**X**) has not been clearly established, however, although Durig and co-workers (DCC) have reported Raman[12] and microwave[14] work on this molecule. In the latter work, three far-infrared absorption bands were also reported. More recently Lopez and co-workers[15] have also carried out a microwave study and determined the ground-state splitting to be 0.012 $cm^{-1}$. Earlier Ueda and Shimanouchi[16] had reported mid-infrared combination band studies. As will be shown in our present work, the previous assignments and published potential energy function need revision.

We have recently reinvestigated the far-infrared spectrum of 2,5-dihydrothiophene[17] (**V**) and utilized it to determine both one- and two-dimensional potential energy surfaces associated with the ring-puckering vibration. We now present here our far-infrared and Raman results for the asymmetric 2,3-dihydrothiophene (**X**). Thanks to the observation of dozens of ring-puckering bands involving single, double, triple, quadruple, and quintuple quantum transition, an accurate potential energy function and barrier to planarity are determined for the first time.

## Experimental Section

The sample of 2,3-dihydrothiophene was prepared and purified by the method of Birch and McAllan.[18] Far-infrared spectra were recorded using a Digilab FTS-20E spectrometer with a helium cooled bolometer detector. Resolutions of 0.125 and 0.25 $cm^{-1}$ were used and 500 to 1000 scans were collected. Samples were contained in a Wilkes variable long-path cell with variable path lengths of 4 to 20 m. Raman spectra of the vapor were recorded using a Model 5 Ramalog 14018 SPEX spectrometer and a Coherent argon ion laser.

## Results and Discussion

**Analysis of Spectra.** Figure 1 shows the far-infrared spectrum of 2,3-dihydrothiophene (**X**) in the 50 to 350 $cm^{-1}$ region. The single quantum transitions ($\Delta v_P = 1$) can be seen at 167.4 $cm^{-1}$ ($1 \rightarrow 2$), 132.7 $cm^{-1}$ ($3 \rightarrow 4$) and between 67.1 and 119.7 $cm^{-1}$. These are summarized in Table 1 where they are also compared to the previous assignments.[14,16] The assignments are readily verified by the observation of the many $\Delta v_P = 2$ bands between 104.7 and 244.6 $cm^{-1}$, the $\Delta v_P = 3$ bands between 152.2 and 360.7 $cm^{-1}$, the $\Delta v_P = 4$ bands between 238.2 and 329.0 $cm^{-1}$, and the $\Delta v_P = 5$ bands between 305.3 and 405.6 $cm^{-1}$. Although

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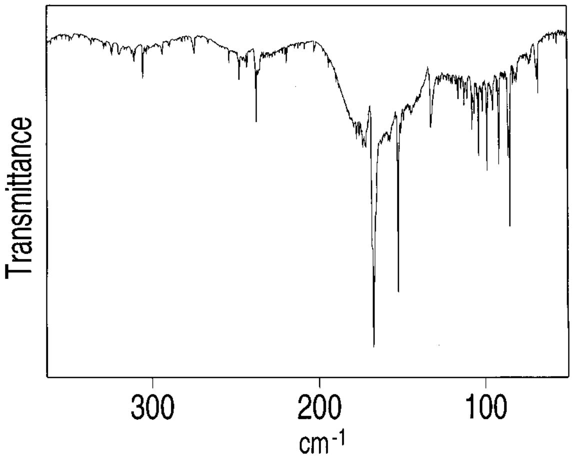

**Figure 1.** Far-infrared spectrum of 2,3-dihydrothiophene. Vapor pressure, 2 Torr; path length, 5 m; resolution, 0.125 cm$^{-1}$.

**TABLE 1: Far-Infrared Spectrum of $\Delta v_P = 1$ Transitions for 2,3-Dihydrothiophene**

| transition | observed | US[c] | DLL[d] |
|---|---|---|---|
| 0−1 | 0.012[a] | | |
| 1−2 | 167.4 | 110.1 | 152 |
| 2−3 | (0.8)[b] | | 15 |
| 3−4 | 132.7 | 62.8 | 100 |
| 4−5 | (18.8)[b] | 54.3 | 45 |
| 5−6 | 85.8 | 68.6 | 86 |
| 6−7 | 67.1 | 80.5 | 88 |
| 7−8 | 84.7 | 89.7 | 99 |
| 8−9 | 91.3 | | |
| 9−10 | 98.6 | | |
| 10−11 | 103.8 | | |
| 11−12 | 108.0 | | |
| 12−13 | 112.5 | | |
| 13−14 | 116.3 | | |
| 14−15 | 119.7 | | |

[a] Reference 15. [b] Inferred from double and triple quantum jumps. [c] Reference 16. [d] Reference 14.

$\Delta v_P = 2$ and 3 transitions have been observed previously for a number of other molecules, the presence of the $\Delta v_P = 4$ and 5 transitions for 2,3-dihydrothiophene is highly unusual. These can be accounted for by the lack of symmetry of the molecule and by the high quality of the spectra reported here. These are tabulated in Table 2. Only bands at 167 (1→ 2), 152 (2 → 5), and 85 cm$^{-1}$ (5 →6 and 7→ 8) were previously reported,[14] but these were misassigned. Figure 2 shows the ring-puckering spectrum expanded in the 65 to 180 cm$^{-1}$ region showing also some of the weaker puckering bands which arise from the ring-twisting excited state ($v_T = 1$). These are tabulated in Table 3. Figure 3 shows the Raman spectrum of the vapor of 2,3-dihydrothiophene, and Table 4 tabulates the observed frequencies and compares them to values previously reported by DCC,[12] as well as to values inferred from the far-infrared assignments. Six of the seven Raman frequencies reported by DCC agree within 3 cm$^{-1}$ of our values, but the assignment can be seen to be completely different. Figure 4 shows the infrared absorption spectrum in the 370 to 430 cm$^{-1}$ region. The strong band at 400.1 cm$^{-1}$ arises from the ring-twisting mode ($v_T = 0 \rightarrow 1$) for $\Delta v_P = 0$ for $v_P = 0$ and 1. For more symmetric molecules, such as I to VII,[5] this band is infrared forbidden (or nearly forbidden) but for the asymmetric 2,3-dihydrothiophene, it is quite strong. The weaker sidebands arise from $\Delta v_P = 0$ transitions for $v_P = 2-6$ and these are listed in Table 5. Weak bands at 405.6 and 389.3 cm$^{-1}$ in this region arise from the 1 → 6 and 3 → 8 transitions, respectively. The observation of the ring-twisting bands ($v_T = 0 \rightarrow 1$, $\Delta v_P = 0$) for $v_P = 0$, 1, 2, 3, 4, 5, and 6 confirms the ring-puckering assignments for the $v_T = 1$ ring-twisting excited state given in Table 3. Figure 5 shows the energy diagram for the ring puckering in the $v_T = 0$ and 1 states. A number of the transitions are also shown.

**TABLE 2: Multiple Quantum Transitions for 2,3-Dihydrothiophene**

| | transition | observed | inferred[a] |
|---|---|---|---|
| $\Delta v_P = 2$ | 0−2 | 167.4 | 167.4 |
| | 1−3 | 168.2[b] | 168.2 |
| | 2−4 | 133.7 | 133.5 |
| | 3−5 | 151.7[b] | 151.5 |
| | 4−6 | 104.7 | 104.6 |
| | 5−7 | 152.6 sh | 152.9 |
| | 6−8 | 151.7[b] | 151.8 |
| | 7−9 | 175.8 | 176.0 |
| | 8−10 | 189.7 | 189.9 |
| | 9−11 | 202.2 | 202.4 |
| | 10−12 | 211.2 | 211.8 |
| | 11−13 | 220.1 | 220.5 |
| | 12−14 | 229.5 | 228.8 |
| | 13−15 | 235.6 | 236.0 |
| | 14−16 | 244.6 | 244.4 |
| $\Delta v_P = 3$ | 0−3 | 168.2[b] | 168.2 |
| | 1−4 | ∼301 | 300.9 |
| | 2−5 | 152.2 | 152.3 |
| | 3−6 | 237.5[b] | 237.7 |
| | 4−7 | 171.7 | 171.7 |
| | 5−8 | 237.5[b] | 237.6 |
| | 6−9 | 243.2 | 243.1 |
| | 7−10 | 274.6 | 274.6 |
| | 8−11 | 293.4 | 293.7 |
| | 9−12 | 310.4 | 310.4 |
| | 10−13 | 324.4 | 324.3 |
| | 11−14 | 336.5 | 336.8 |
| | 12−15 | 348.5 | 348.5 |
| | 13−16 | 360.7 | 360.7 |
| $\Delta v_P = 4$ | 0−4 | ∼301 | 300.9 |
| | 1−5 | 319.8[b] | 319.7 |
| | 2−6 | 238.2 | 238.1 |
| | 3−7 | 303.7 | 304.4 |
| | 4−8 | | 356.4 |
| | 5−9 | 329.0 | 328.8 |
| $\Delta v_P = 5$ | 0−5 | 319.8[b] | 319.7 |
| | 1−6 | 405.6 | 405.5 |
| | 2−7 | 305.3 | 305.2 |
| | 3−8 | 389.3 | 389.1 |
| | 4−9 | 348.5 | 347.7 |

[a] From $\Delta v_P = 1$ frequencies. [b] Assignment used twice.

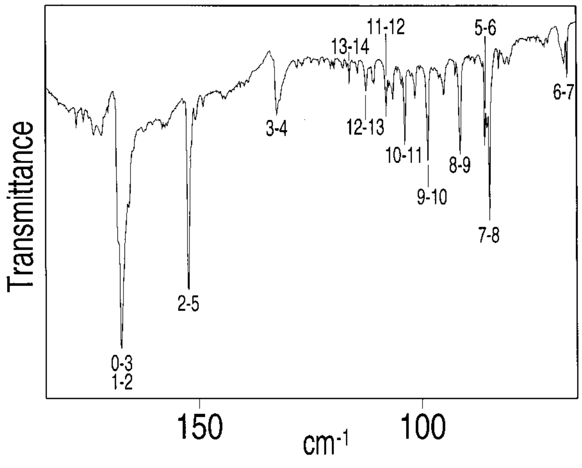

**Figure 2.** Expanded far-infrared spectrum of 2,3-dihydrothiophene.

**Calculation of Potential Energy Surfaces.** The data presented above and summarized in Figure 5 was utilized to determine the potential energy surfaces. First, the kinetic energy

**TABLE 3: Ring-Puckering Transitions ($cm^{-1}$) for the Ring-Twisting ($v_T = 1$) Excited State**

| transition | frequency ($v_T = 1$) | ground state ($v_T = 0$) |
|---|---|---|
| 0−1 | (0.01)[a] | 0.012 |
| 1−2 | 165.7 | 167.4 |
| 2−3 | (0.8)[b] | (0.8)[b] |
| 3−4 | 128.0 | 132.7 |
| 4−5 | 22.0 | 18.8 |
| 5−6 | 82.7 | 85.8 |
| 6−7 | 67.7 | 67.1 |
| 7−8 | 85.3 | 84.7 |
| 8−9 | 92.5 | 91.3 |
| 9−10 | 99.0 | 98.6 |
| 2−5 | 150.8 | 152.3 |
| 3−6 | 232.7 | 237.6 |
| 5−8 | 235.6 | 237.5 |

[a] Calculated. [b] Inferred from other transition frequencies.

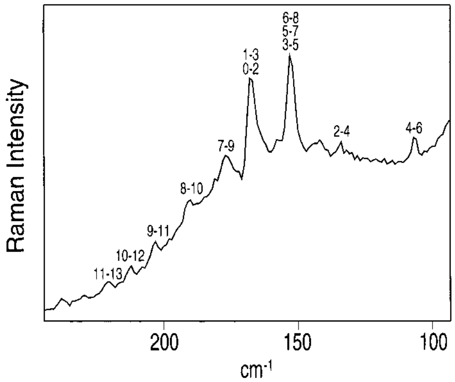

**Figure 3.** Raman spectrum of 2,3-dihydrothiophene at 110°. Resolution: 2 $cm^{-1}$.

**TABLE 4: Raman Spectra of the Ring-Puckering of 2,3-Dihydrothiophene**

| transition | this work | DCC[a] | inferred[b] |
|---|---|---|---|
| 0−2 | 167.4 | 151.1 | 167.4 |
| 1−3 | 167.4 | 165.6 | 168.2 |
| 2−4 | 133.4 | 105.0 | 133.5 |
| 3−5 | 152.4[c] | 145.1 | 151.5 |
| 4−6 | 105.5 | 131.3 | 104.6 |
| 5−7 | 152.4[c] | 174.5 | 152.9 |
| 6−8 | 152.4[c] | 187.5 | 151.8 |
| 7−9 | 176.1 | | 176.0 |
| 8−10 | 189.9 | | 189.9 |
| 9−11 | 202.7 | | 202.4 |
| 10−12 | 211.7 | | 211.8 |
| 11−13 | 220.4 | | 220.5 |

[a] Reference 12; the reported wavenumbers when reassigned to the correct transition are typically ~2 $cm^{-1}$ lower than those reported in "this work". A weak band at 142 $cm^{-1}$ observed in the present work may correspond to the DCC 145.1 $cm^{-1}$ value. [b] From far-infrared data. [c] The 152.4 $cm^{-1}$ band has contributions from the 3 → 5, 5 → 7, and 6 → 8 transitions expected at 151.5, 152.9, 151.8 $cm^{-1}$, respectively.

(reciprocal reduced mass) function was calculated for the ring-puckering vibration ($x_1$) using methods previously described.[19] The coordinate $x_1$ is essentially half the distance between ring diagonals and this is defined in terms of the structural parameters as presented elsewhere.[19] The structural parameters were obtained from an *ab initio* calculation at the HF/6-31+G* level, and these are shown in Figure 6. The kinetic energy function was determined to be

$$g_{44}(x_1) = 0.0082713 - 0.025358x_1^2 - 0.088040x_1^4 + 0.41417x_1^6 \quad (1)$$

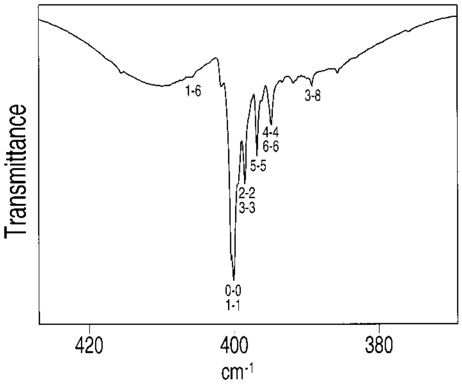

**Figure 4.** Infrared spectrum of 2,3-dihydrothiophene in the ring-twisting region.

**TABLE 5: Ring-Twisting Infrared Hot Bands ($cm^{-1}$) of 2,3-Dihydrothiophene**

| transition[a] | observed | inferred[b] |
|---|---|---|
| 0−0 | 400.1 | 400.1 |
| 1−1 | 400.1 | 400.1 |
| 2−2 | 398.5 | 398.4 |
| 3−3 | 398.5 | 398.4 |
| 4−4 | 394.9 | 393.7 |
| 5−5 | 396.8 | 396.9 |
| 6−6 | 394.9 | 393.8 |

[a] $v_P$ values shown for $v_T = 0 \rightarrow 1$. [b] From data in Table 3.

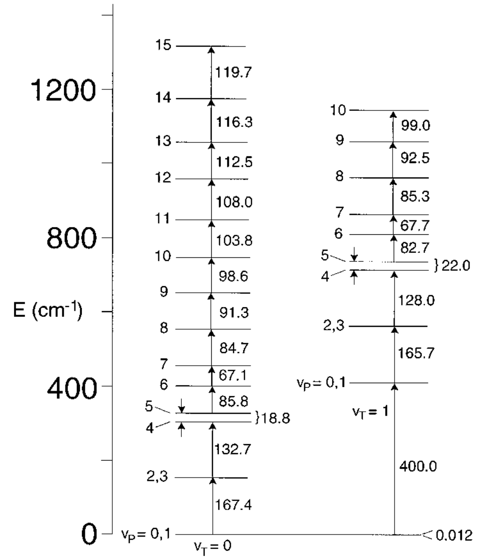

**Figure 5.** Energy diagram for the ring-puckering levels in the $v_T = 0$ and 1 ring-twisting states.

The one-dimensional potential energy function was then determined utilizing our computational methodology[2−5] and the Hamiltonian

$$H = -(\hbar^2/2)\partial/\partial x_1 g_{44}(x_1)\partial/\partial x_1 + V(x_1) \quad (2)$$

The potential energy function was found to be

$$V(cm^{-1}) = 6.557 \times 10^5 x_1^4 - 3.357 \times 10^4 x_1^2 \quad (3)$$

This has a barrier to planarity of 430 $cm^{-1}$ with minima for the puckering coordinate at $x_1 = \pm 0.16$ Å which correspond to dihedral angles of bending of 31°. Figure 7 shows this potential energy function along with the observed transitions. In the ring-twisting excited state ($v_T = 1$), this potential function has a

**TABLE 6: Observed and Calculated Ring-Puckering Frequencies ($cm^{-1}$) and Intensities for One- and Two-Dimensional Potential Energy Surfaces**

| | observed | | | 1-DIM[a] | | 2-DIM[b] | |
|---|---|---|---|---|---|---|---|
| | transition | $v$ | intensity | $v$ | intensity | $v$ | intensity |
| $v_T = 0$ | 0−1 | 0.012[c] | | 0.010 | | 0.010 | |
| | 1−2 | 167.4 | (1.0) | 167.5 | (1.0) | 167.6 | (1.0) |
| | 2−3 | (0.8)[d] | | 0.8 | | 0.8 | |
| | 3−4 | 132.7 | 0.2 | 132.4 | 0.7 | 132.4 | 0.7 |
| | 4−5 | (18.8)[d] | | 18.3 | 0.06 | 18.3 | 0.06 |
| | 5−6 | 85.8 | 0.4 | 84.6 | 0.5 | 84.5 | 0.5 |
| | 6−7 | 67.1 | 0.3 | 66.9 | 0.3 | 66.9 | 0.3 |
| | 7−8 | 84.7 | 1.0 | 84.7 | 0.4 | 84.7 | 0.4 |
| | 8−9 | 91.3 | 0.4 | 90.5 | 0.3 | 90.5 | 0.3 |
| | 9−10 | 98.6 | 0.4 | 97.3 | 0.3 | 97.4 | 0.3 |
| | 10−11 | 103.8 | 0.4 | 103.0 | 0.2 | 103.0 | 0.2 |
| | 11−12 | 108.0 | 0.3 | 108.2 | 0.1 | 108.2 | 0.1 |
| | 12−13 | 112.5 | 0.1 | 112.9 | 0.1 | 112.9 | 0.1 |
| | 13−14 | 116.3 | 0.1 | 117.2 | 0.06 | 117.3 | 0.06 |
| | 14−15 | 119.7 | 0.06 | 121.3 | 0.04 | 121.4 | 0.04 |
| | 0−3 | 168.1 | 0.4 | 168.4 | 1.0 | 168.4 | 1.0 |
| $v_T = 1$ | 0−1 | (0.0)[d] | | 0.01 | | 0.01 | |
| | 1−2 | 165.0 | 0.2 | 165.7 | (0.2) | 165.6 | 0.15 |
| | 2−3 | (0.8)[d] | | 1.1 | | 1.1 | |
| | 3−4 | 128.0 | 0.05 | 128.2 | 0.14 | 128.2 | 0.10 |
| | 4−5 | (22.0)[d] | | 21.3 | 0.02 | 21.2 | 0.01 |
| | 5−6 | 82.7 | 0.1 | 82.8 | 0.10 | 82.7 | 0.08 |
| | 6−7 | 67.7 | 0.1 | 69.5 | 0.08 | 69.4 | 0.06 |
| | 7−8 | 85.3 | 0.1 | 85.5 | 0.09 | 85.4 | 0.06 |
| | 8−9 | 92.5 | 0.06 | 91.6 | 0.08 | 91.5 | 0.05 |
| | 9−10 | 99.0 | 0.03 | 98.2 | 0.06 | 98.1 | 0.04 |

[a] $V = 6.557 \times 10^5 x_1^4 - 3.357 \times 10^4 x_1^2$ for $v_T = 0$. $V = 6.549 \times 10^5 x_1^4 - 3.296 \times 10^4 x_1^2$ for $v_T = 1$. [b] $V = 6.588 \times 10^5 x_1^4 - 3.384 \times 10^4 x_1^2 + 5.744 \times 10^4 x_2^2 + 1.709 \times 10^5 x_1^2 x_2^2$. [c] Reference 15. [d] Inferred from $\Delta v_P = 2, 3, 4$, and 5 transitions.

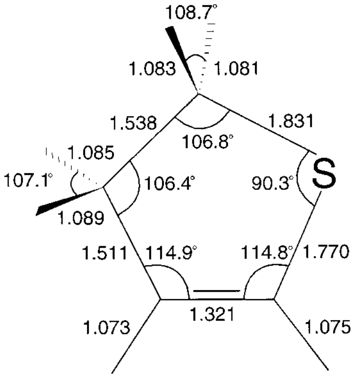

**Figure 6.** Calculated structure for 2,3-dihydrothiophene. The dihedral angle of puckering is calculated to be 29°.

barrier of 415 $cm^{-1}$ and the form

$$V(\text{cm}^{-1}) = 6.549 \times 10^5 x_1^4 - 3.296 \times 10^4 x_1^2 \qquad (4)$$

The calculated transition frequencies and relative intensities for the potential energy functions given in eqs 3 and 4 are compared to the observed values in Table 6. The agreement can be seen to be excellent with an average difference of about 0.4 $cm^{-1}$.

The ring-puckering frequency changes in the ring-twisting excited state, which is 400.1 $cm^{-1}$ above the ground state, result from the interaction between the puckering and twisting motions. This can be taken into account with a two-dimensional potential energy surface using the puckering ($x_1$) and twisting ($x_2$) coordinates for the calculation. We recently carried out a similar calculation for 2,5-dihydrothiophene.[17] For 2,3-dihydrothiophene the $g_{55}(x_2)$ reciprocal mass value was calculated to be 0.038588 $au^{-1}$ by taking the average of values computed for the symmetric cyclopentene and the $\overline{\text{SCH}_2\text{SCH}{=}\text{CH}}$ molecules. The two-dimensional function determined for these two modes is

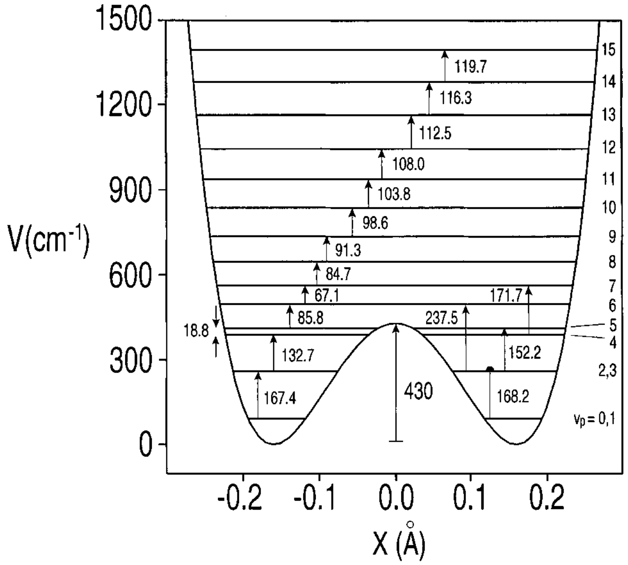

**Figure 7.** One-dimensional potential energy function for the ring puckering of 2,3-dihydrothiophene.

$$V(\text{cm}^{-1}) = 6.588 \times 10^5 x_1^4 - 3.384 \times 10^4 x_1^2 + 5.744 \times 10^4 x_2^2 + 1.709 \times 10^5 x_1^2 x_2^2 \qquad (5)$$

which corresponds to a barrier to planarity of 435 $cm^{-1}$. The energy minima are again at $x_1 = \pm 0.16$ Å or a dihedral angle of 31°. The calculated frequency values for this potential energy surface are shown also in Table 6, and the frequency fit can be seen to be almost identically as good as for the two independent one-dimensional fits. Figure 8 shows this two-dimensional surface. This calculation results in an interaction term of $1.67 \times 10^5$ $cm^{-1}/Å^4$ for 2,3-dihydrothiophene. The magnitude is somewhat higher than the $1.39 \times 10^5$ $cm^{-1}/Å^4$ value found

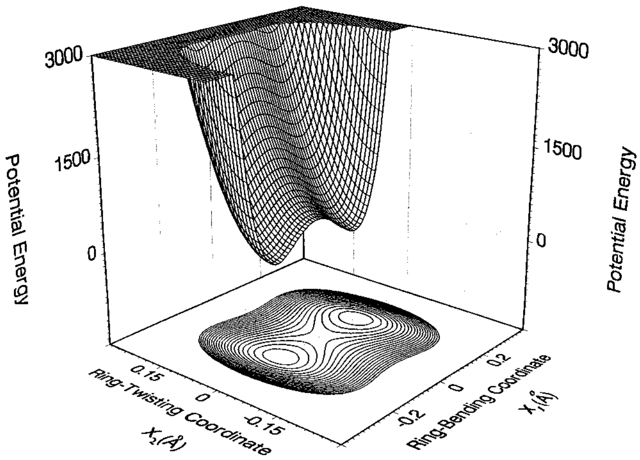

**Figure 8.** Two-dimensional potential energy function for the ring puckering and ring twisting of 2,3-dihydrothiophene.

for 2,5-dihydrothiophene. The increase is expected as the asymmetry of the 2,3 compound allows for greater interaction between these two modes. It should be noted that for these calculations the cross kinetic energy term ($g_{45}$) was assumed to be zero although the molecular asymmetry for the molecule does lead to a small nonzero magnitude for this term.

## Conclusions

The barrier to planarity of 2,3-dihydrothiophene has been accurately determined for the first time. Previous studies were shown to have incorrect assignments. The barrier to planarity calculated for the one-dimensional model is 430 $\text{cm}^{-1}$, while it is 435 $\text{cm}^{-1}$ for the two-dimensional model. Since the interaction between the puckering and twisting is present, the latter value can be taken to be the actual barrier. The molecule has a dihedral angle of puckering of 31°. Our *ab initio* calculation gave a dihedral angle of 29°. While the results here show the earlier infrared and Raman assignments[12] to be wrong, they are totally consistent with the more recent microwave results which determined the ground-state splitting to be 0.012 $\text{cm}^{-1}$.

As compared to 2,3-dihydrofuran, which has a barrier to planarity of 83 $\text{cm}^{-1}$ and a dihedral angle of 22°, 2,3-dihydrothiophene is considerably more puckered. This clearly results from the presence of the sulfur atom and the relatively small value of the CSC angle bending force constant. The resultant lower angle strain allows the $-CH_2-CH_2-$ torsional interaction to dominate and the molecule to pucker to a greater degree.

The magnitude of the interaction constant between the puckering and twisting that was determined was found to be similar to that for cyclopentene[6] ($1.90 \times 10$ $\text{cm}^{-1}/\text{Å}^4$), silacyclopent-3-ene[20] ($1.70 \times 10^5$ $\text{cm}^{-1}/\text{Å}^4$), 2,5-dihydrofuran[16,20] ($2.23 \times 10^5 \text{cm}^{-1}/\text{Å}^4$), and 2,5-dihydrothiophene[17] ($1.39 \times 10^5$ $\text{cm}^{-1}/\text{Å}^4$). These interactions do appear to increase with increased angle strain, however, and thus are smaller for the rings containing the larger and "softer" sulfur or silicon atoms.

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## References and Notes

(1) Carreira, L. A.; Lord, R. C.; Malloy, T. B. *Top. Curr. Chem.* **1979**, *82*, 1.
(2) Laane, J. *Pure Appl. Chem.* **1987**, *59*, 1307.
(3) Laane, J. *Structures and Conformations of Non-Rigid Molecules*; Laane, J., Dakkouri, M., van der Veken, B., Oberhammer, H., Eds.; Kluwer: London, 1993.
(4) Laane, J. *Annu. Rev. Phys. Chem.* **1994**, *45*, 179.
(5) Laane, J. *Int. Rev. Phys. Chem.* **1999**, *18*, 301.
(6) Bauman, L. E.; Killough, P. M.; Cooke, J. M.; Villarreal, J. R.; Laane, J. *J. Phys. Chem.* **1982**, *86*, 2000 and references therein.
(7) Cortez, E.; Verastegui, R.; Villarreal, J. R.; Laane, J. *J. Am. Chem. Soc.* **1991**, *115*, 12132.
(8) Cheatham, C. M.; Laane, J. *J. Chem. Phys.* **1991**, *94*, 5394.
(9) Laane, J. *J. Chem. Phys.* **1970**, *52*, 358.
(10) Kelly, M. B.; Laane, J. *J. Phys. Chem.* **1988**, *92*, 4056.
(11) Green, W. H. *J. Chem. Phys.* **1969**, *50*, 1619.
(12) Durig, J. R.; Carter, R. O.; Carreira, L. A. *J. Chem. Phys.* **1974**, *59*, 2249.
(13) Lopez, J. C.; Wloderczak, G.; Demaison, J. *J. Mol Spectrosc.* **1996**, *180*, 337.
(14) Durig, J. R.; Little, T. S.; Li, Y. S. *J. Chem. Phys.* **1982**, *76*, 3849.
(15) Lopez, J. C.; Esposti, A. D.; Lister, D. G.; Cervellati, R.; Alonso, J. L.; Forlani, L *J. Mol. Struct.* **1986**, *142*, 97.
(16) Ueda, T.; Shimanouchi, T. *J. Chem. Phys* **1967**, *47*, 5018.
(17) Klots, T.; Lee, S. N.; Laane J. *J. Phys. Chem.* **1999**, *103*, 833.
(18) Birch, S. F.; McAllan, D. T. *J. Chem. Soc.* **1951**, 2556.
(19) Schmude, R. W.; Harthcock, M. A.; Kelly, M. B. *J. Mol. Spectrosc.* **1987**, *124*, 1987.
(20) Killough, P. M.; Laane, J. *J. Chem. Phys.* **1984**, *80*, 5475.
(21) Carreira, L. A.; Mills, I. M.; Person, W. B. *J. Chem. Phys.* **1972**, *56*, 1444.