Hydrogen-atom tunneling through a very high barrier; spontaneous thiol $\rightarrow$ thione conversion in thiourea isolated in low-temperature Ar, Ne, H$_2$ and D$_2$ matrices

Hanna Rostkowska, Leszek Lapinski and Maciej J. Nowak

Electronic Supplementary Information
Fig. S1 Infrared spectra of thiourea monomers isolated in a Ne matrix. The spectra were recorded: (b) after deposition of the matrix, the spectrum of the thione tautomer; (c) after UV (λ > 270 nm) irradiation of the matrix, when the thiol tautomers were generated. The experimental spectra are compared with (a) theoretical spectrum calculated at the DFT(B3LYP)/6-311++G(2d,p) level for thione form of thiourea. The calculated wavenumbers were scaled by 0.98.
**Fig. S2** Infrared spectrum of the photoproducts generated (see Fig. S1) upon UV(λ > 270 nm) irradiation of monomers of thiourea isolated in a Ne matrix. The experimental spectrum (a) is compared with theoretical spectra calculated at the DFT(B3LYP)/6-311++G(2d,p) level for $t11$ (b, green) and $t12$ (c, blue) thiol conformers of thiourea. The calculated wavenumbers were scaled by 0.98.
**Fig. S3** The barriers for the tl4 → tl1 and tl3 → tl2 rotamerization, calculated at the MP2/6-311++G(2d,p) level. The calculated energy of tl4 form is 6.8 kJmol\(^{-1}\) higher than tl1, and the height of the barrier for tl4 → tl1 transition is 11.2 kJmol\(^{-1}\). The Red asterisk shows the position of the optimized tl3→tl2 transition state TS. The calculated energy of TS is higher by 9.4 kJmol\(^{-1}\) than the energy of tl2 form.
Fig. S4 Thiol → thione (tl1 → tn) tunneling transformation observed for monomers of thiourea isolated in a Ne matrix. The thiol tl1 and tl2 forms of the compound were prepared upon UV (λ > 270 nm) irradiation. The IR spectrum of the UV-irradiated matrix is shown as trace (b, red). The matrix was then kept for 48 hours at 3.5 K and in the dark. The IR spectrum recorded after this long period is presented in trace (c, black). The tunneling process revealed itself as intensity decrease of IR bands due to tl1 and intensity increase of the bands due to tn, see trace (d, blue) where the difference spectrum: trace c minus trace b is shown. The experimental bands assigned to UV-generated thiol form tl2 did not change their intensities proving that this conformer was not involved in any spontaneous structural alterations. Fragments of the IR spectrum of tl2, calculated at the DFT(B3LYP)/6-311++G(2d,p) level, are shown in trace (a). The calculated wavenumbers were scaled by 0.98.
**Fig. S5** Barrier for the thiol → thione (tl1 → tn) transition in thiourea. The barrier was calculated, at the MP2/6-311++G(2d,p) level, as a relaxed scan. At each point of this scan the S-H distance (left panel) or N-H distance (right panel) was fixed at a chosen value and all other parameters determining the geometry of the molecule were fully optimized. The highest-energy point of the barrier (marked with an asterisk) corresponds to the optimized transition state. Zero on the ordinate scale corresponds to the energy calculated for the tn tautomer. The calculated energy of tl1 is higher by 62 kJ mol\(^{-1}\) and the energy of the transition state is higher by 166 kJ mol\(^{-1}\) than the energy of tn,
**Fig. S6** Fragment of the near-IR spectra of thiourea isolated in an Ar matrix: (a) recorded after deposition of the matrix; (b) recorded after UV(λ > 270 nm) irradiation of the matrix. After exposure to UV light the matrix was additionally irradiated with monochromatic near-IR light from a tunable diode laser at wavenumbers indicated by the arrows.
Table S1. Experimental wavenumbers ($\nu$) and relative integrated intensities ($I$) of the IR absorption bands in the spectrum of thiourea isolated in Ar, D$_2$, H$_2$ and Ne matrices and the tentative assignment to the normal modes calculated for thione form $tn$.

<table>
<thead>
<tr>
<th>Mode number$^a$</th>
<th>Ar matrix $\nu$ / cm$^{-1}$</th>
<th>$I$ / rel.</th>
<th>D$_2$ matrix $\nu$ / cm$^{-1}$</th>
<th>$I$ / rel.</th>
<th>H$_2$ matrix $\nu$ / cm$^{-1}$</th>
<th>$I$ / rel.</th>
<th>Ne matrix $\nu$ / cm$^{-1}$</th>
<th>$I$ / rel.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q_{tn1}$, $Q_{tn2}$</td>
<td>3539</td>
<td>172</td>
<td>3545</td>
<td>122</td>
<td>3546</td>
<td>118</td>
<td>3557</td>
<td>124</td>
</tr>
<tr>
<td>$Q_{tn3}$</td>
<td>3424</td>
<td>47</td>
<td>3431</td>
<td>23</td>
<td>3432</td>
<td>28</td>
<td>3437</td>
<td>36</td>
</tr>
<tr>
<td>$Q_{tn4}$</td>
<td>3418</td>
<td>67</td>
<td>3424</td>
<td>64</td>
<td>3425</td>
<td>79</td>
<td>3437</td>
<td>86</td>
</tr>
<tr>
<td>$Q_{tn5}$</td>
<td>1610</td>
<td>71</td>
<td>1613</td>
<td>72</td>
<td>1612</td>
<td>83</td>
<td>1614</td>
<td>90</td>
</tr>
<tr>
<td>$Q_{tn6}$</td>
<td>1590, 1581</td>
<td>152</td>
<td>1592</td>
<td>247</td>
<td>1593</td>
<td>224</td>
<td>1589</td>
<td>243</td>
</tr>
<tr>
<td>$Q_{tn7}$</td>
<td>1518</td>
<td>6</td>
<td>1517</td>
<td>4</td>
<td>1518</td>
<td>6</td>
<td>1526</td>
<td>4</td>
</tr>
<tr>
<td>$Q_{tn8}$</td>
<td>1401</td>
<td>96</td>
<td>1413</td>
<td>80</td>
<td>1412</td>
<td>84</td>
<td>1404</td>
<td>87</td>
</tr>
<tr>
<td>$Q_{tn9}$</td>
<td>1389, 1385</td>
<td>384</td>
<td>1391</td>
<td>352</td>
<td>1391</td>
<td>352</td>
<td>1394</td>
<td>306</td>
</tr>
<tr>
<td>$Q_{tn10}$</td>
<td>1273</td>
<td>1</td>
<td>1282, 1274</td>
<td>2</td>
<td>1282, 1274</td>
<td>3</td>
<td>1270</td>
<td>1</td>
</tr>
<tr>
<td>$Q_{tn11}$</td>
<td>1192</td>
<td>9</td>
<td>1210</td>
<td>7</td>
<td>1204</td>
<td>6</td>
<td>1194</td>
<td>11</td>
</tr>
<tr>
<td>$Q_{tn12}$</td>
<td>1078</td>
<td>7</td>
<td>1091</td>
<td>3</td>
<td>1088</td>
<td>3</td>
<td>1081</td>
<td>8</td>
</tr>
<tr>
<td>$Q_{tn13}$</td>
<td>1043</td>
<td>74</td>
<td>1051</td>
<td>63</td>
<td>1050</td>
<td>68</td>
<td>1045</td>
<td>77</td>
</tr>
<tr>
<td>$Q_{tn14}$</td>
<td>1024</td>
<td>12</td>
<td>1036</td>
<td>10</td>
<td>1032</td>
<td>13</td>
<td>1027</td>
<td>13</td>
</tr>
<tr>
<td>$Q_{tn15}$</td>
<td>760</td>
<td>16</td>
<td>759</td>
<td>16</td>
<td>759</td>
<td>16</td>
<td>764</td>
<td>17</td>
</tr>
<tr>
<td>$Q_{tn16}$</td>
<td>712</td>
<td>28</td>
<td>743</td>
<td>7</td>
<td>749</td>
<td>20</td>
<td>721</td>
<td>20</td>
</tr>
<tr>
<td>$Q_{tn17}$</td>
<td>645</td>
<td>29</td>
<td>~700</td>
<td>12</td>
<td>688</td>
<td>12</td>
<td>640</td>
<td>4</td>
</tr>
<tr>
<td>$Q_{tn18}$</td>
<td>578</td>
<td>22</td>
<td>574</td>
<td>10</td>
<td>567</td>
<td>7</td>
<td>561</td>
<td>11</td>
</tr>
</tbody>
</table>

Wavenumbers of more intense components of split bands are underline.

$^a$ Frequencies and intensities of normal modes calculated at the DFT(B3LYP)/6-311++G(2d,p) level for the thione tautomer $tn$ of thiourea are given in Table S4 of the ESI.
Table S2. Experimental wavenumbers ($\nu$) and relative integrated intensities ($I$) of the IR absorption bands in the spectrum of the photoproduc t generated upon UV irradiation of thiourea isolated in low-temperature matrices, tentatively assigned to the normal modes calculated for the thiol t11 isomer of thiourea.

<table>
<thead>
<tr>
<th>Mode number$^a$</th>
<th>Ar matrix</th>
<th>D$_2$ matrix</th>
<th>H$_2$ matrix</th>
<th>Ne matrix</th>
<th>Mode number$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu$ / cm$^{-1}$</td>
<td>$I$ / rel.</td>
<td>$\nu$ / cm$^{-1}$</td>
<td>$I$ / rel.</td>
<td>$\nu$ / cm$^{-1}$</td>
</tr>
<tr>
<td>Q$_{11}$1</td>
<td>3520</td>
<td>68</td>
<td>3527</td>
<td>39</td>
<td>3529</td>
</tr>
<tr>
<td>Q$_{11}$2</td>
<td>3419</td>
<td>27</td>
<td>3426</td>
<td>13</td>
<td>3427</td>
</tr>
<tr>
<td>Q$_{11}$4</td>
<td>2625</td>
<td>13</td>
<td>2620</td>
<td>10</td>
<td>2619</td>
</tr>
<tr>
<td>Q$_{11}$5</td>
<td>1641</td>
<td>293</td>
<td>1642</td>
<td>312</td>
<td>1642</td>
</tr>
<tr>
<td>Q$_{11}$6</td>
<td>1597</td>
<td>68</td>
<td>1599</td>
<td>72</td>
<td>1599</td>
</tr>
<tr>
<td>Q$_{11}$7</td>
<td></td>
<td></td>
<td>1398</td>
<td>10</td>
<td>1399</td>
</tr>
<tr>
<td>Q$_{11}$8</td>
<td>1342</td>
<td>26</td>
<td>1348</td>
<td>24</td>
<td>1348</td>
</tr>
<tr>
<td>Q$_{11}$9</td>
<td>1318</td>
<td>187</td>
<td>1325</td>
<td>145</td>
<td>1325</td>
</tr>
<tr>
<td>Q$_{11}$10</td>
<td>1086</td>
<td>44</td>
<td>1092</td>
<td>43</td>
<td>1092</td>
</tr>
<tr>
<td>Q$_{11}$11</td>
<td>1067</td>
<td>48</td>
<td>1073</td>
<td>54</td>
<td>1073</td>
</tr>
<tr>
<td>Q$_{11}$12</td>
<td>890, 888</td>
<td>16</td>
<td>894</td>
<td>20</td>
<td>894</td>
</tr>
<tr>
<td>Q$_{11}$13</td>
<td>807</td>
<td>34</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Q$_{11}$14</td>
<td>772</td>
<td>25</td>
<td>784</td>
<td>55</td>
<td>783</td>
</tr>
<tr>
<td>Q$_{11}$15</td>
<td>671</td>
<td>53</td>
<td>674</td>
<td>65</td>
<td>674</td>
</tr>
<tr>
<td>Q$_{11}$16</td>
<td>586</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Wavenumbers of more intense components of split bands are underlined.

$^a$ Frequencies and intensities of normal modes calculated at the DFT(B3LYP)/6-311++G(2d,p) level for the thiol t11 isomer of thiourea are given in Table S5 of the ESI.
Table S3. Experimental wavenumbers ($\nu$) and relative integrated intensities ($I$) of the IR absorption bands in the spectrum of the photoproduct generated upon UV irradiation of thiourea isolated in low-temperature matrices, tentatively assigned to the normal modes calculated for the thiol $\text{tl}_2$ isomer of thiourea.

<table>
<thead>
<tr>
<th>Ar matrix</th>
<th>$\nu$ / cm$^{-1}$</th>
<th>$I$ / rel.</th>
<th>$\nu$ / cm$^{-1}$</th>
<th>$I$ / rel.</th>
<th>$\nu$ / cm$^{-1}$</th>
<th>$I$ / rel.</th>
<th>$\nu$ / cm$^{-1}$</th>
<th>$I$ / rel.</th>
<th>Mode number$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3522</td>
<td>84</td>
<td>3522</td>
<td>134</td>
<td>3525</td>
<td>80</td>
<td>3540</td>
<td>55</td>
<td>Q$_{\text{tl}_2}^1$</td>
<td></td>
</tr>
<tr>
<td>3415</td>
<td>39</td>
<td>3433</td>
<td>59</td>
<td>Q$_{\text{tl}_2}^2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2623</td>
<td>6</td>
<td>2618</td>
<td>3</td>
<td>Q$_{\text{tl}_2}^4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1649</td>
<td>327</td>
<td>1651</td>
<td>192</td>
<td>1652</td>
<td>235</td>
<td>1659</td>
<td>323</td>
<td>Q$_{\text{tl}_2}^5$</td>
<td></td>
</tr>
<tr>
<td>1580</td>
<td>40</td>
<td>1585</td>
<td>64</td>
<td>Q$_{\text{tl}_2}^6$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1445</td>
<td>2</td>
<td>1451</td>
<td>28</td>
<td>1451</td>
<td>147</td>
<td>1451</td>
<td>22</td>
<td>Q$_{\text{tl}_2}^7$</td>
<td></td>
</tr>
<tr>
<td>1294</td>
<td>149</td>
<td>1300</td>
<td>78</td>
<td>1300</td>
<td>106</td>
<td>1301, 1297</td>
<td>104</td>
<td>Q$_{\text{tl}_2}^7$</td>
<td></td>
</tr>
<tr>
<td>1121, 1112</td>
<td>80</td>
<td>1122</td>
<td>55</td>
<td>Q$_{\text{tl}_2}^8$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1077</td>
<td>59</td>
<td>1084</td>
<td>59</td>
<td>1084</td>
<td>186</td>
<td>1080</td>
<td>108</td>
<td>Q$_{\text{tl}_2}^9$</td>
<td></td>
</tr>
<tr>
<td>909</td>
<td>16</td>
<td>913</td>
<td>16</td>
<td>913</td>
<td>26</td>
<td>912</td>
<td>13</td>
<td>Q$_{\text{tl}_2}^{10}$</td>
<td></td>
</tr>
<tr>
<td>829</td>
<td>6</td>
<td>818</td>
<td>43</td>
<td>Q$_{\text{tl}_2}^{11}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>658</td>
<td>35</td>
<td>755</td>
<td>39</td>
<td>Q$_{\text{tl}_2}^{12}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Frequencies and intensities of normal modes calculated at the DFT(B3LYP)/6-311++G(2d,p) level for the thiol $\text{tl}_2$ isomer of thiourea are given in Table S6 of the ESI.
Table S4. Normal mode frequencies ($\tilde{\nu}$) and absolute intensities ($A^\text{th}$) of the IR bands predicted at the DFT(B3LYP)/6-311++G(2d,p) level for the thione tautomer tn of thiourea.

<table>
<thead>
<tr>
<th>mode number</th>
<th>$\tilde{\nu}$ (x0.98) / cm$^{-1}$</th>
<th>$A^\text{th}$ / km mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Qtn1</td>
<td>3611</td>
<td>24</td>
</tr>
<tr>
<td>Qtn2</td>
<td>3610</td>
<td>67</td>
</tr>
<tr>
<td>Qtn3</td>
<td>3490</td>
<td>12</td>
</tr>
<tr>
<td>Qtn4</td>
<td>3482</td>
<td>43</td>
</tr>
<tr>
<td>Qtn5</td>
<td>1620</td>
<td>72</td>
</tr>
<tr>
<td>Qtn6</td>
<td>1595</td>
<td>207</td>
</tr>
<tr>
<td>Qtn7</td>
<td>1387</td>
<td>102</td>
</tr>
<tr>
<td>Qtn8</td>
<td>1379</td>
<td>300</td>
</tr>
<tr>
<td>Qtn9</td>
<td>1051</td>
<td>22</td>
</tr>
<tr>
<td>Qtn10</td>
<td>1041</td>
<td>75</td>
</tr>
<tr>
<td>Qtn11</td>
<td>749</td>
<td>11</td>
</tr>
<tr>
<td>Qtn12</td>
<td>627</td>
<td>6</td>
</tr>
<tr>
<td>Qtn13</td>
<td>565</td>
<td>90</td>
</tr>
<tr>
<td>Qtn14</td>
<td>488</td>
<td>45</td>
</tr>
<tr>
<td>Qtn15</td>
<td>450</td>
<td>4</td>
</tr>
<tr>
<td>Qtn16</td>
<td>392</td>
<td>2</td>
</tr>
<tr>
<td>Qtn17</td>
<td>381</td>
<td>308</td>
</tr>
<tr>
<td>Qtn18</td>
<td>333</td>
<td>126</td>
</tr>
</tbody>
</table>
Table S5. Normal mode frequencies (ν̃) and absolute intensities (A\textsuperscript{th}) of the IR bands predicted at the DFT(B3LYP)/6-311++G(2d,p) level for the thiol tl1 isomer of thiourea.

<table>
<thead>
<tr>
<th>mode number</th>
<th>ν̃ (x0.98) / cm\textsuperscript{-1}</th>
<th>A\textsuperscript{th} / km mol\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q₁₁₁₁</td>
<td>3586</td>
<td>25</td>
</tr>
<tr>
<td>Q₁₁₁₂</td>
<td>3484</td>
<td>25</td>
</tr>
<tr>
<td>Q₁₁₁₃</td>
<td>3386</td>
<td>5</td>
</tr>
<tr>
<td>Q₁₁₁₄</td>
<td>2646</td>
<td>4</td>
</tr>
<tr>
<td>Q₁₁₁₅</td>
<td>1649</td>
<td>303</td>
</tr>
<tr>
<td>Q₁₁₁₆</td>
<td>1609</td>
<td>75</td>
</tr>
<tr>
<td>Q₁₁₁₇</td>
<td>1312</td>
<td>154</td>
</tr>
<tr>
<td>Q₁₁₁₈</td>
<td>1090</td>
<td>16</td>
</tr>
<tr>
<td>Q₁₁₁₉</td>
<td>1058</td>
<td>87</td>
</tr>
<tr>
<td>Q₁₁₁₁₀</td>
<td>888</td>
<td>19</td>
</tr>
<tr>
<td>Q₁₁₁₁₁</td>
<td>774</td>
<td>81</td>
</tr>
<tr>
<td>Q₁₁₁₁₂</td>
<td>648</td>
<td>66</td>
</tr>
<tr>
<td>Q₁₁₁₁₃</td>
<td>589</td>
<td>5</td>
</tr>
<tr>
<td>Q₁₁₁₁₄</td>
<td>474</td>
<td>231</td>
</tr>
<tr>
<td>Q₁₁₁₁₅</td>
<td>448</td>
<td>9</td>
</tr>
<tr>
<td>Q₁₁₁₁₆</td>
<td>375</td>
<td>14</td>
</tr>
<tr>
<td>Q₁₁₁₁₇</td>
<td>350</td>
<td>10</td>
</tr>
<tr>
<td>Q₁₁₁₁₈</td>
<td>184</td>
<td>24</td>
</tr>
</tbody>
</table>
Table S6. Normal mode frequencies ($\tilde{\nu}$) and absolute intensities ($A^\text{th}$) of the IR bands predicted at the DFT(B3LYP)/6-311++G(2d,p) level for the thiol tl2 isomer of thiourea.

<table>
<thead>
<tr>
<th>Mode Number</th>
<th>Frequency (x0.98) / cm$^{-1}$</th>
<th>Intensity / km mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q_{tl2}1</td>
<td>3594</td>
<td>34</td>
</tr>
<tr>
<td>Q_{tl2}2</td>
<td>3483</td>
<td>30</td>
</tr>
<tr>
<td>Q_{tl2}3</td>
<td>3472</td>
<td>16</td>
</tr>
<tr>
<td>Q_{tl2}4</td>
<td>2637</td>
<td>1</td>
</tr>
<tr>
<td>Q_{tl2}5</td>
<td>1661</td>
<td>288</td>
</tr>
<tr>
<td>Q_{tl2}6</td>
<td>1586</td>
<td>67</td>
</tr>
<tr>
<td>Q_{tl2}7</td>
<td>1296</td>
<td>214</td>
</tr>
<tr>
<td>Q_{tl2}8</td>
<td>1122</td>
<td>63</td>
</tr>
<tr>
<td>Q_{tl2}9</td>
<td>1068</td>
<td>85</td>
</tr>
<tr>
<td>Q_{tl2}10</td>
<td>910</td>
<td>13</td>
</tr>
<tr>
<td>Q_{tl2}11</td>
<td>765</td>
<td>30</td>
</tr>
<tr>
<td>Q_{tl2}12</td>
<td>641</td>
<td>39</td>
</tr>
<tr>
<td>Q_{tl2}13</td>
<td>624</td>
<td>117</td>
</tr>
<tr>
<td>Q_{tl2}14</td>
<td>516</td>
<td>181</td>
</tr>
<tr>
<td>Q_{tl2}15</td>
<td>433</td>
<td>16</td>
</tr>
<tr>
<td>Q_{tl2}16</td>
<td>404</td>
<td>37</td>
</tr>
<tr>
<td>Q_{tl2}17</td>
<td>349</td>
<td>1</td>
</tr>
<tr>
<td>Q_{tl2}18</td>
<td>216</td>
<td>15</td>
</tr>
</tbody>
</table>