

# Supporting Information

**Title:** Time-Resolved Resonance Raman Observation of the Dimerization of Didehydroazepines in Solution

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**Description of Contents:** **Figure 1S** shows an overview of the 341.5 nm probe TR<sup>3</sup> spectra obtained after 266 nm photolysis of ~3 mM 3-hydroxyphenyl azide in a water: acetonitrile (50: 50) solvent. **Figure 2S** shows 341.5 nm probe TR<sup>3</sup> spectra obtained after 266 nm photolysis of ~3 mM 3-nitrophenyl azide in acetonitrile. **Figure 3S** shows 341.5 nm probe TR<sup>3</sup> spectra obtained after 266 nm photolysis of ~3 mM phenyl azide in acetonitrile. **Figure 4S** shows 341.5 nm probe TR<sup>3</sup> spectra obtained after 266 nm photolysis of ~3 mM 3-hydroxyphenyl azide in acetonitrile. **Figure 5S** shows 341.5 nm probe TR<sup>3</sup> spectra obtained after 266 nm photolysis of ~3 mM 3-hydroxyphenyl azide in a water: acetonitrile (95:5) solvent. **Figure 6S** shows 341.5 nm probe TR<sup>3</sup> spectra obtained after 266 nm photolysis of ~3 mM 3-methoxyphenyl azide in acetonitrile. **Figure 7S** shows a comparison of the experimental 50  $\mu$ s TR<sup>3</sup> spectrum from Figure 3 obtained after photolysis of 3-hydroxyphenyl azide to the B3LYP/6-31G\* calculated normal Raman spectra for the 3-hydroxy substituted didehydroazepine dimer possible structures. **Figure 8S** shows a comparison of the experimental 50  $\mu$ s TR<sup>3</sup> spectrum obtained after photolysis of 3-hydroxyphenyl azide in a water: acetonitrile (50: 50) solution to that obtained in acetonitrile. **Figure 9S:** Comparison of the experimental 50  $\mu$ s TR<sup>3</sup> spectrum from Figure 2 obtained after photolysis of phenyl azide to the B3LYP/6-31G\* calculated normal Raman spectra for the didehydroazepine dimers. **Figure 10S:** Comparison of the experimental 50  $\mu$ s TR<sup>3</sup> spectrum from Figure 2 obtained after photolysis of 3-methoxyphenyl azide to the B3LYP/6-31G\* calculated normal Raman spectra for the 3-methoxy substituted didehydroazepine dimers. **TABLE 1S** compares the B3LYP/6-31G\* calculated Raman vibrational frequencies for 3,3'-dinitroazobenzene to those observed for the 50  $\mu$ s TR<sup>3</sup> experimental spectrum of Figure 1 obtained after photolysis of 3-nitrophenyl azide. **TABLES 2S, 3S and 4S** compare the B3LYP/6-31G\* calculated Raman vibrational frequencies for the didehydroazepine dimers to those observed for the 50  $\mu$ s TR<sup>3</sup> experimental spectra of Figures 2-4 obtained after photolysis of phenyl azide, 3-hydroxyphenyl azide and 3-methoxyphenyl azide in a water: acetonitrile (50:50) solvent respectively. **TABLE 5S** compare the B3LYP/6-31G\* calculated Raman vibrational frequencies for the ketone isomer to those observed for the 50  $\mu$ s TR<sup>3</sup> experimental spectrum of Figure 3 obtained after photolysis of 3-hydroxyphenyl azide in water: acetonitrile (50:50). Cartesian coordinates, total energies, and vibrational zero-point energies for the optimized geometry from the B3LYP/6-31G\* calculations for the 3, 3'-dinitroazobenzene, the didehydroazepine dimer, the 3-hydroxy didehydroazepine substituted dimers and its corresponding ketone dimer, and the 3-methoxy substituted didehydroazepine dimers investigated in this work.

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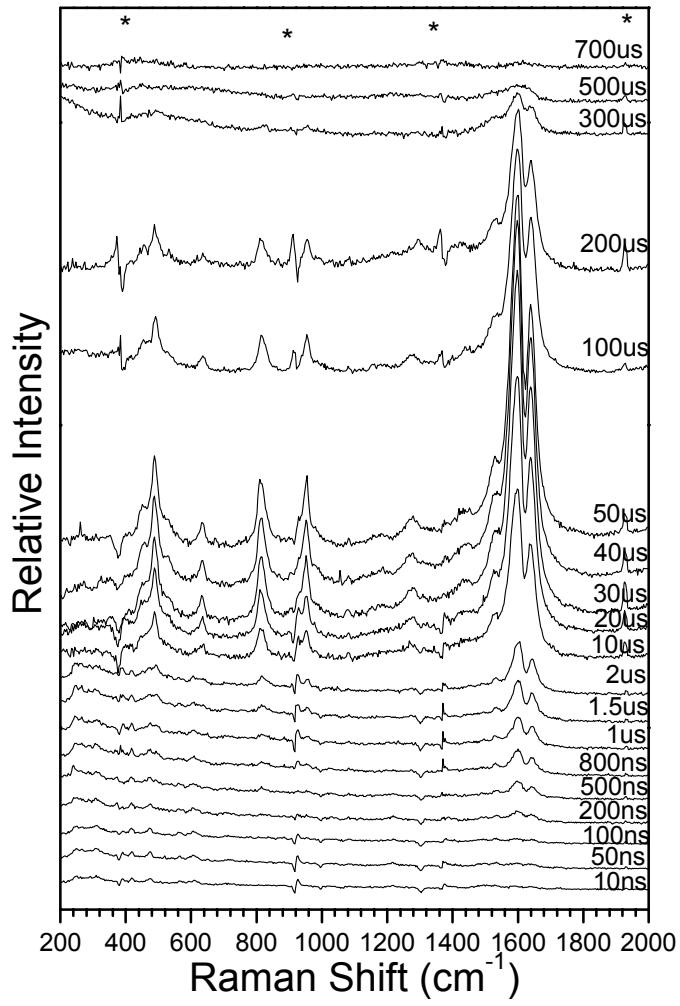
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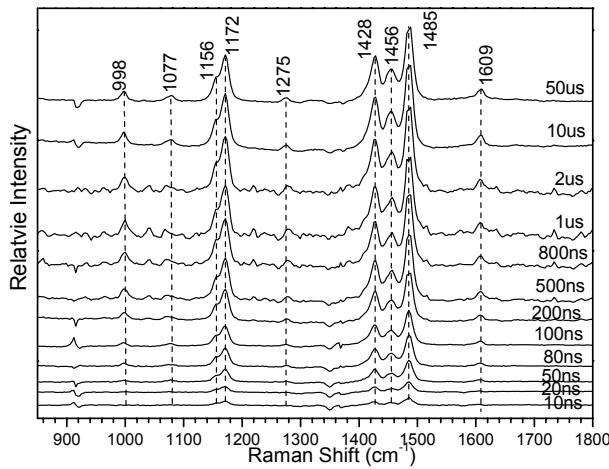
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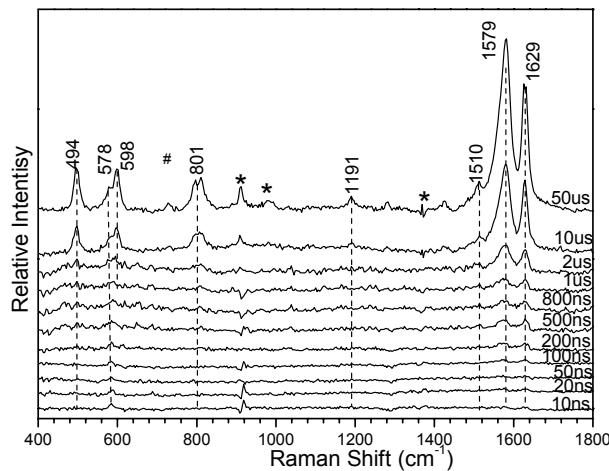
Cartesian coordinates, total energies, and vibrational zero-point energies for the optimized geometry from the B3LYP/6-31G\* calculations for the 3, 3'-dinitroazobenzene, the didehydroazepine dimer, the 3-hydroxy substituted didehydroazepine dimers and its corresponding ketone dimer, and the 3-methoxy substituted didehydroazepine dimers investigated in this work. S16-S120



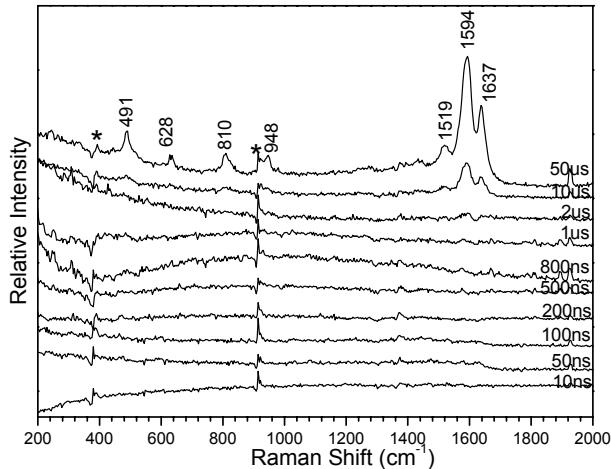
**Figure 1S.** Overview of 341.5 nm probe TR<sup>3</sup> spectra obtained after 266 nm photolysis of ~3 mM 3-hydroxyphenyl azide in a water:acetonitrile (50:50) solution. The time delays between the pump (266 nm) and probe (341.5 ns) laser beams are shown to the right of each spectrum. Star symbols mark solvent-subtraction artifacts, stray-light artifacts.



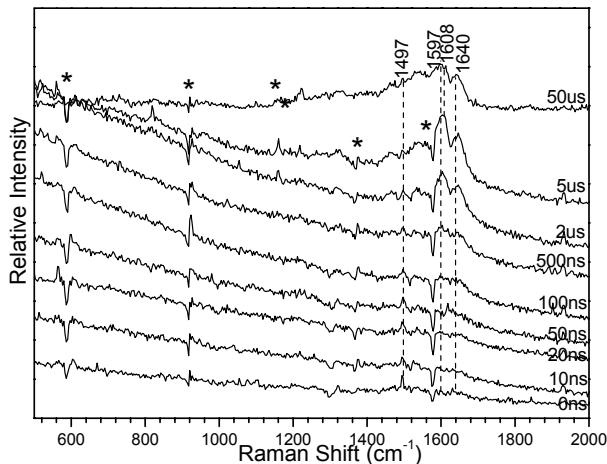
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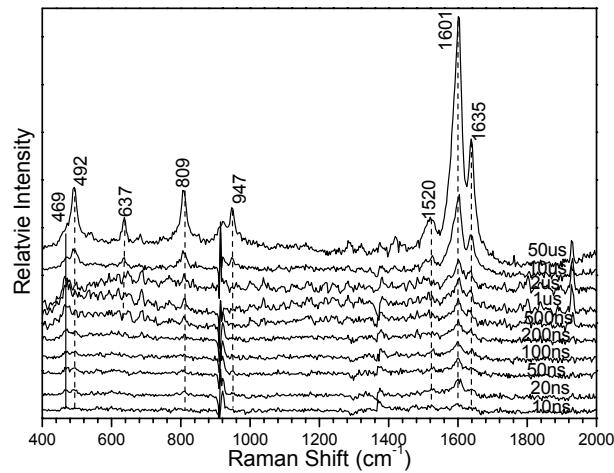
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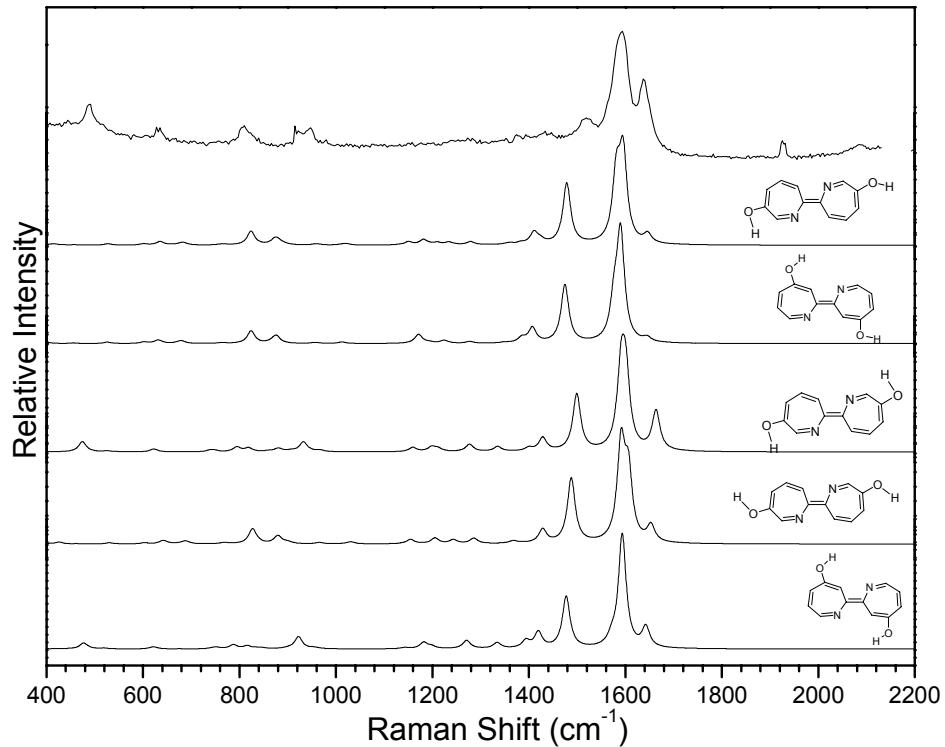
**Figure 4S.**  $\text{TR}^3$  spectra obtained using a 341.5 nm probe beam after 266 nm photolysis of  $\sim 3$  mM 3-hydroxyphenyl azide in acetonitrile. The time delays between the pump (266 nm) and probe (341.5 nm) laser beams are shown to the right of each spectrum and the Raman shifts of selected bands are presented at the top of the 50  $\mu\text{s}$  spectrum. Star symbols mark solvent-subtraction artifacts, stray-light artifacts. See text for more details.



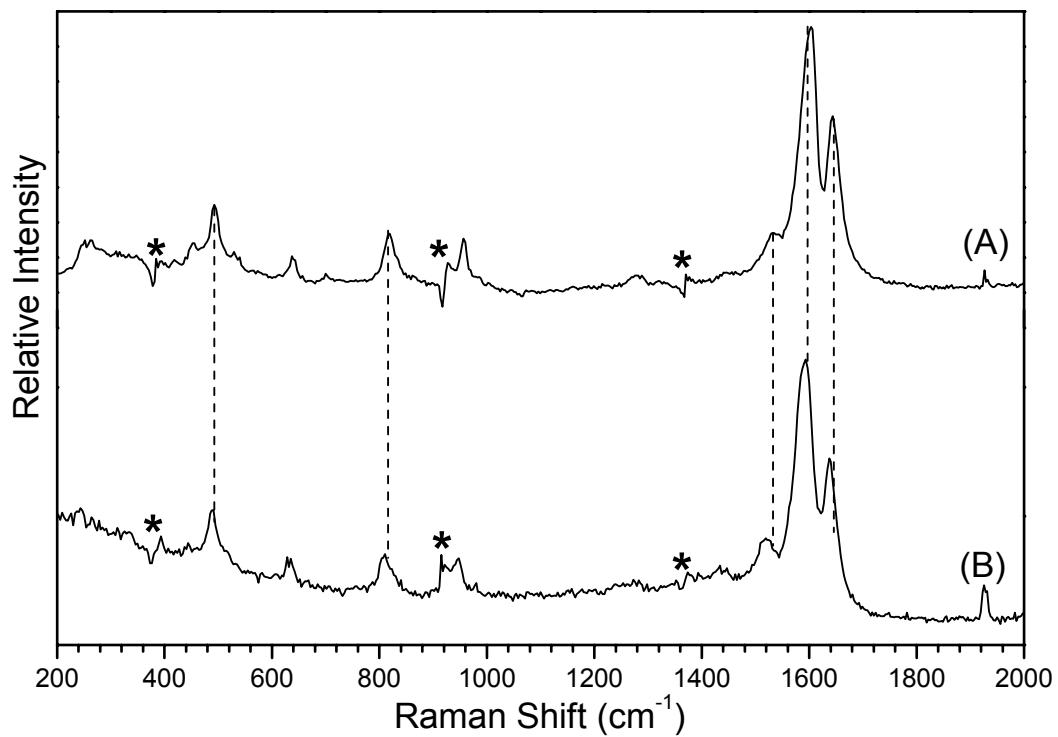
**Figure 5S.**  $\text{TR}^3$  spectra obtained by a 341.5 nm probe beam after 266 nm photolysis of  $\sim 3$  mM 3-hydroxyphenyl azide in water: acetonitrile (95: 5) solution. The time delays between the pump (266 nm) and probe (341.5 nm) laser beams are shown to the right of each spectrum and the Raman shifts of selected bands are presented at the top of the 50  $\mu\text{s}$  spectrum. Star symbols mark solvent-subtraction artifacts, stray-light artifacts. See text for more details.



**Figure 6S.**  $\text{TR}^3$  spectra by a 341.5 nm probe beam after 266 nm photolysis of ~3 mM 3-methoxyphenyl azide in acetonitrile. The time delays between the pump (266 nm) and probe (341.5 nm) laser beams are shown to the right of each spectrum and the Raman shifts of selected bands are presented at the top of the 50  $\mu\text{s}$  spectrum. See text for more details.

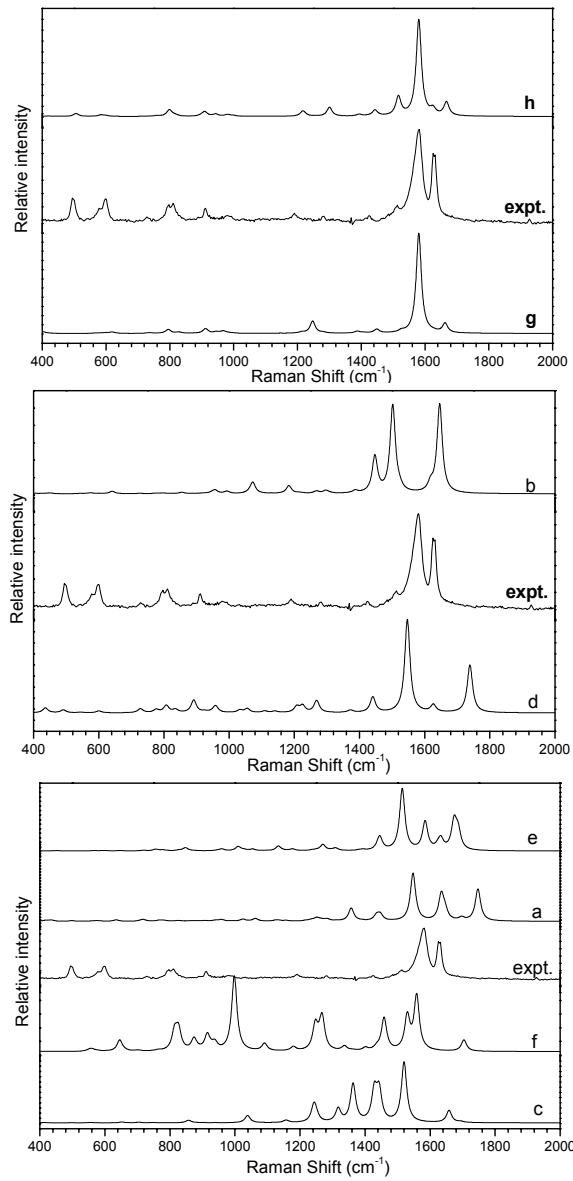


**Figure 7S:** Comparison of the experimental  $50 \mu\text{s}$  TR<sup>3</sup> spectrum from Figure 3 obtained after photolysis of 3-hydroxyphenyl azide to the B3LYP/6-31G\* calculated normal Raman spectra for the 3-hydroxy substituted didehydroazepine dimers, whose structures are displayed next the calculated spectra. Star symbols mark solvent-subtraction artifacts, stray-light and ambient-light artifacts.

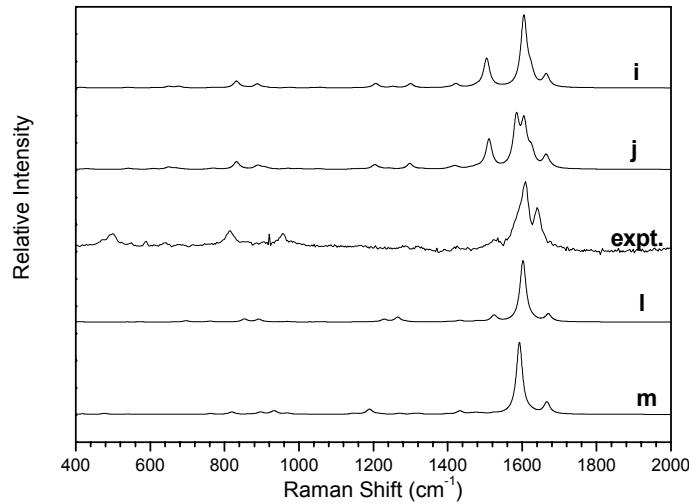


**Figure 8S.** Comparison of the experimental 50  $\mu\text{s}$  TR<sup>3</sup> spectrum obtained after photolysis of 3-hydroxyphenyl azide (A) in a water: acetonitrile (50: 50) solution to (B) in acetonitrile.

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**Figure 9S:** Comparison of the experimental 50  $\mu$ s TR<sup>3</sup> spectrum from Figure 2 obtained after photolysis of phenyl azide to the B3LYP/6-31G\* calculated normal Raman spectra for the didehydroazepine dimers.



**Figure 10S:** Comparison of the experimental 50  $\mu$ s TR<sup>3</sup> spectrum from Figure 2 obtained after photolysis of 3-methoxyphenyl azide to the B3LYP/6-31G\* calculated normal Raman spectra for the 3-methoxy substituted didehydroazepine dimers.

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**TABLE 1S:** Comparison of the B3LYP/6-31G\* calculated Raman vibrational frequencies for 3, 3'-dinitroazobenzene to those observed for the 50  $\mu$ s TR<sup>3</sup> experimental spectrum of Figure 1 obtained after photolysis of 3-nitrophenyl azide<sup>a</sup>

Vibrational mode possible description	Calc.	B3LYP/6-31G*		Expt.
	Raman Activity	Frequencies calc.(cm <sup>-1</sup> )	Raman Shift (cm <sup>-1</sup> )	
<b>v<sub>45</sub></b> CCC bend		<b>979</b>	<b>249</b>	<b>998</b>
v <sub>46</sub> C-H bend + C-N stretch		1056	80	
v <sub>47</sub> C-H bend + C-N stretch		1058	180	
v <sub>48</sub> C-H bend		1070	4	
<b>v<sub>49</sub></b> C-H bend + C-N stretch		<b>1071</b>	<b>41</b>	<b>1080</b>
v <sub>50</sub> C-H bend + C-N stretch		1143	749	
v <sub>51</sub> C-H bend + C-N stretch		1144	16	
<b>v<sub>52</sub></b> C-N stretch		<b>1156</b>	<b>2167</b>	<b>1155</b>
<b>v<sub>53</sub></b> C-N stretch (symmetry)		<b>1201</b>	<b>3</b>	<b>1172</b>
v <sub>54</sub> C-H bend		1256	94	
<b>v<sub>55</sub></b> C-H bend + C-N stretch		<b>1264</b>	<b>113</b>	<b>1279</b>
v <sub>56</sub> C-C stretch		1325	46	
<b>v<sub>57</sub></b> C-C stretch		1330	92	
<b>v<sub>58</sub></b> C-(NO <sub>2</sub> ) stretch		1344	116	
v <sub>59</sub> C-(NO <sub>2</sub> ) stretch		1347	209	
v <sub>60</sub> C-H bend + C-C stretch		1417	1135	
<b>v<sub>61</sub></b> C-H bend + C-C stretch		<b>1422</b>	<b>182</b>	<b>1429</b>
<b>v<sub>62</sub></b> C-H bend + C-N stretch + N=N stretch		<b>1450</b>	<b>935</b>	<b>1456</b>
<b>v<sub>63</sub></b> C-H bend + C-N stretch + C-C stretch		<b>1459</b>	<b>17</b>	
<b>v<sub>64</sub></b> C-C stretch + N=N stretch		<b>1502</b>	<b>3731</b>	<b>1486</b>
v <sub>65</sub> C-C stretch + N-O stretch		1562	2	
v <sub>66</sub> C-C stretch + N-O stretch		1569	51	
<b>v<sub>67</sub></b> C-C stretch + N=N stretch		1574	34	
v <sub>68</sub> C-C stretch + N=N stretch		1580	147	
<b>v<sub>69</sub></b> C-C stretch + N=N stretch + N-O stretch		<b>1612</b>	<b>43</b>	
<b>v<sub>70</sub></b> C-C stretch + N=N stretch + N-O stretch		<b>1615</b>	<b>207</b>	<b>1610</b>

<sup>a</sup> Experimental vibrational frequencies are compared to those from B3LYP/6-31G\* calculations for the 3, 3'-dinitroazobenzene. See text for more details. Possible vibrational band assignments are also shown based on comparison to the calculated vibrational frequencies from the B3LYP/6-31G\* calculations in the 1000-1700 cm<sup>-1</sup> fingerprint region for 3, 3'-dinitroazobenzene.

**TABLE 2S:** Comparison of the B3LYP/6-31G\* calculated Raman vibrational frequencies for the didehydroazepine dimer to those observed for the 50  $\mu$ s TR<sup>3</sup> experimental spectrum of Figure 2 obtained after photolysis of phenyl azide in a water: acetonitrile (50:50) solution.

Vibrational mode possible description	Calc.	B3LYP/6-31G*	Expt.
	Raman Activity	Frequencies calc.(cm <sup>-1</sup> )	Raman Shift (cm <sup>-1</sup> )
v <sub>10</sub> ring deformation	6	405	
v <sub>11</sub> ring deformation	6	421	
v <sub>12</sub> ring deformation	2	421	
v <sub>13</sub> ring deformation	1	449	
<b>v<sub>14</sub> ring deformation + C-H bend</b>	<b>84</b>	<b>506</b>	<b>498</b>
v <sub>15</sub> ring deformation + C-H bend	2	560	
<b>v<sub>16</sub> ring deformation</b>	<b>42</b>	<b>584</b>	<b>585</b>
<b>v<sub>17</sub> ring deformation</b>	<b>22</b>	<b>599</b>	<b>605</b>
<b>v<sub>18</sub> ring deformation + C-H bend</b>	<b>2</b>	<b>604</b>	
v <sub>19</sub> C-H bend	3	738	
v <sub>20</sub> ring deformation + C-H bend	17	757	
v <sub>21</sub> C-H bend	7	790	
<b>v<sub>22</sub> ring deformation + C-H bend</b>	<b>185</b>	<b>799</b>	<b>806</b>
v <sub>23</sub> ring deformation + C-H bend	26	814	
v <sub>24</sub> ring deformation	12	821	
v <sub>25</sub> ring deformation	1	890	
v <sub>36</sub> C-H bend + NCC bend	7	1000	
v <sub>37</sub> C-H bend + C-C bend (bridge)	15	1000	
v <sub>38</sub> C-H bend + C-N stretch	1	1147	
<b>v<sub>39</sub> C-H bend + C-N stretch</b>	<b>141</b>	<b>1217</b>	<b>1187</b>
v <sub>40</sub> C-H bend	1	1223	
v <sub>41</sub> C-H bend	22	1223	
v <sub>42</sub> C-H bend + C-N stretch	2	1256	
v <sub>43</sub> C-H bend + C-C stretch (ring)	259	1300	
v <sub>44</sub> C-H bend	50	1393	
v <sub>45</sub> C-H bend	0	1396	
v <sub>46</sub> C-H bend	5	1417	
v <sub>47</sub> C-H bend + C-N stretch	0	1423	
v <sub>48</sub> C-H bend + C-N stretch	165	1443	
v <sub>49</sub> C-H bend	4	1454	
<b>v<sub>50</sub> C=C stretch (bridge)</b>	<b>544</b>	<b>1516</b>	<b>1519</b>
<b>v<sub>51</sub> C-C aromatic stretch + C=C stretch (bridge)</b>	<b>2739</b>	<b>1580</b>	<b>1582</b>
<b>v<sub>52</sub> C-C aromatic stretch</b>	<b>49</b>	<b>1582</b>	
<b>v<sub>53</sub> C=N stretch + C=C stretch (ring)</b>	<b>4</b>	<b>1624</b>	
<b>v<sub>54</sub> C=N stretch + C=C stretch (ring)</b>	<b>169</b>	<b>1625</b>	<b>1629</b>
v <sub>55</sub> C=N stretch + C=C stretch (ring)	391	1667	
v <sub>56</sub> C=N stretch + C=C stretch (ring)	0	1677	

**TABLE 3S:** Comparison of the B3LYP/6-31G\* calculated Raman vibrational frequencies for 3-hydroxy substituted didehydroazepine dimer to those observed for the 50  $\mu$ s TR<sup>3</sup> experimental spectrum of Figure 3 obtained after photolysis of 3-hydroxyphenyl azide in a water: acetonitrile (50:50) solution.

Vibrational mode possible description	Calc.		Expt.
	Raman	B3LYP/6-31G*	Raman
	Activity	Frequencies calc.(cm <sup>-1</sup> )	Shift (cm <sup>-1</sup> )
v <sub>15</sub> ring deformation	1	408	
v <sub>16</sub> ring deformation + O-H bend	3	423	
v <sub>17</sub> ring deformation + O-H bend	8	450	
v <sub>18</sub> ring deformation	2	464	
<b>v<sub>19</sub> ring deformation + C-H bend</b>	<b>142</b>	<b>484</b>	<b>473</b>
<b>v<sub>20</sub> ring deformation + C-Obend</b>	<b>4</b>	<b>495</b>	<b>493</b>
v <sub>21</sub> ring deformation	15	531	
v <sub>22</sub> ring deformation + C-H bend	3	550	
<b>v<sub>23</sub> ring deformation + C-H bend + O-H bend</b>	<b>47</b>	<b>632</b>	<b>608/637</b>
v <sub>24</sub> ring deformation + C-H bend	4	685	
v <sub>25</sub> ring deformation	0	723	
<b>v<sub>26</sub> C-H bend + ring deformation</b>	<b>22</b>	<b>752</b>	<b>752</b>
v <sub>27</sub> C-H bend + ring deformation	21	767	
<b>v<sub>28</sub> ring deformation + C-H bend</b>	<b>77</b>	<b>804</b>	<b>807</b>
<b>v<sub>29</sub> ring deformation</b>	<b>5</b>	<b>814</b>	<b>819</b>
<b>v<sub>30</sub> ring deformation</b>	<b>61</b>	<b>832</b>	
v <sub>31</sub> C-H bend +CCC bend	14	856	
v <sub>32</sub> C-H bend +CCC bend	37	882	
v <sub>33</sub> NCC bend + CCC bend + C-H bend	7	915	
v <sub>34</sub> NCC bend + CCC bend + C-H bend	6	919	
v <sub>35</sub> NCC bend + CCC bend	9	924	
<b>v<sub>36</sub> C-H bend + O-H bend + NCC bend + CCC bend</b>	<b>198</b>	<b>943</b>	
<b>v<sub>37</sub> C-H bend + CCC bend</b>	<b>5</b>	<b>957</b>	<b>956</b>
<b>v<sub>38</sub> C-H bend + NCC bend + CCC bend</b>	<b>5</b>	<b>959</b>	
v <sub>39</sub> C-H bend + CCC bend	8	974	
v <sub>40</sub> C-H bend + CCC bend	14	979	
v <sub>41</sub> C-H bend + O-H bend + NCC bend + CCC bend	4	988	
v <sub>54</sub> C-H bend + O-H bend + C=C stretch (bridge, weak)	190	1446	
v <sub>55</sub> C-H bend + O-H bend + C=C stretch (bridge, weak)	77	1459	
<b>v<sub>56</sub> C=C stretch (bridge) + O-H bend</b>	<b>1009</b>	<b>1515</b>	<b>1534</b>
<b>v<sub>57</sub> C=N stretch + C=C stretch (ring, bridge)</b>	<b>419</b>	<b>1601</b>	
<b>v<sub>58</sub> C=N stretch + C=C stretch (ring, bridge)</b>	<b>142</b>	<b>1611</b>	
<b>v<sub>59</sub> C=N stretch + C-C aromatic stretch (ring) + C=C stretch (bridge)</b>	<b>1607</b>	<b>1625</b>	
<b>v<sub>60</sub> C=N stretch + C-C aromatic stretch (ring)</b>	<b>323</b>	<b>1631</b>	<b>1603</b>
v <sub>61</sub> C=N stretch + C=C stretch (ring)	502	1681	
v <sub>62</sub> C=N stretch + C=C stretch (ring)	39	1689	

**TABLE 4S:** Comparison of the B3LYP/6-31G\* calculated Raman vibrational frequencies for 3-methoxy substituted didehydroazepine dimer to those observed for the 50  $\mu$ s TR<sup>3</sup> experimental spectrum of Figure 4 obtained after photolysis of 3-methoxyphenyl azide in a water: acetonitrile (50:50) solution.

Vibrational mode possible description	Calc.	Raman Activity	B3LYP/6-31G* Frequencies calc.(cm <sup>-1</sup> )	Expt. Raman Shift (cm <sup>-1</sup> )
v <sub>18</sub> ring deformation		6	406	
v <sub>19</sub> ring deformation		9	422	
v <sub>20</sub> ring deformation		6	457	
<b>v<sub>21</sub> ring deformation</b>		<b>6</b>	<b>470</b>	<b>472</b>
<b>v<sub>22</sub> ring deformation</b>		<b>30</b>	<b>478</b>	<b>499</b>
<b>v<sub>23</sub> ring deformation + C-H bend</b>		<b>75</b>	<b>512</b>	
v <sub>24</sub> ring deformation		45	523	
v <sub>25</sub> ring deformation		18	543	
v <sub>26</sub> ring deformation + C-H bend		2	572	
<b>v<sub>27</sub> ring deformation + C-H bend</b>		<b>44</b>	<b>648</b>	<b>643</b>
v <sub>28</sub> ring deformation		4	705	
v <sub>29</sub> ring deformation		2	719	
v <sub>30</sub> ring deformation + C-H bend		28	775	
v <sub>31</sub> ring deformation + C-H bend		19	783	
<b>v<sub>32</sub> ring deformation + C-H bend</b>		<b>91</b>	<b>818</b>	<b>815</b>
v <sub>33</sub> ring deformation		23	826	
v <sub>34</sub> ring deformation		63	839	
v <sub>35</sub> C-H bend		11	886	
v <sub>36</sub> C-H bend + NCC bend + CCC bend		85	914	
v <sub>37</sub> C-H bend + NCC bend + CCC bend		24	934	
v <sub>38</sub> NCC bend + C-H bend		16	939	
v <sub>39</sub> NCC bend + CCC bend		20	944	
<b>v<sub>40</sub> NCC bend + CCC bend</b>		<b>179</b>	<b>964</b>	<b>956</b>
v <sub>41</sub> C-H bend + C-C bend (ring)		12	976	
v <sub>42</sub> C-H bend + C-C bend (ring)		17	991	
v <sub>66</sub> CH3 wag		33	1503	
v <sub>67</sub> CH3 wag		26	1507	
<b>v<sub>68</sub> CH3 wag + C=C stretch (bridge, weak)</b>		<b>81</b>	<b>1522</b>	
<b>v<sub>69</sub> CH3 wag + C=C stretch (bridge, weak)</b>		<b>73</b>	<b>1523</b>	<b>1530</b>
<b>v<sub>70</sub> C=C stretch (bridge) + CH3 wag</b>		<b>767</b>	<b>1535</b>	
<b>v<sub>71</sub> C-C aromatic stretch (ring) + C=C stretch (bridge)</b>		<b>1856</b>	<b>1609</b>	<b>1609</b>
<b>v<sub>72</sub> C=N stretch + C=C stretch (ring, bridge)</b>		<b>388</b>	<b>1637</b>	
<b>v<sub>73</sub> C=N stretch + C-C aromatic stretch (ring) + C=C stretch (bridge)</b>		<b>1325</b>	<b>1655</b>	<b>1640</b>
<b>v<sub>74</sub> C=N stretch + C-C aromatic stretch (ring)</b>		<b>29</b>	<b>1658</b>	
v <sub>75</sub> C=N stretch + C=C stretch (ring)		469	1702	
v <sub>76</sub> C=N stretch + C=C stretch (ring)		17	1711	

**TABLE 5S:** Comparison of the B3LYP/6-31G\* calculated Raman vibrational frequencies for ketone isomer to those observed for the 50  $\mu$ s TR<sup>3</sup> experimental spectrum of Figure 3 obtained after photolysis of 3-hydroxyphenyl azide in a water: acetonitrile (50:50) solution.

Vibrational mode possible description	Calc.	B3LYP/6-1G*		Expt.
		Raman Activity	Frequencies calc.(cm <sup>-1</sup> )	Raman Shift (cm <sup>-1</sup> )
v <sub>15</sub> <b>ring deformation</b>		1	<b>468</b>	<b>473</b>
v <sub>16</sub> ring deformation		0	501	
v <sub>17</sub> <b>C=C bend (bridge)</b>		<b>68</b>	<b>504</b>	<b>493</b>
v <sub>18</sub> ring deformation		7	537	
v <sub>19</sub> CH2 wag + C-H bend + CNC bend		1	556	
v <sub>20</sub> <b>ring deformation + C-H bend</b>		<b>40</b>	<b>593</b>	<b>608</b>
v <sub>21</sub> <b>ring deformation</b>		<b>286</b>	<b>644</b>	<b>637</b>
v <sub>22</sub> ring deformation + C-H bend		4	691	
v <sub>23</sub> CCC bend		2	708	
v <sub>24</sub> <b>C-H bend + CNC bend</b>		<b>2</b>	<b>758</b>	<b>752</b>
v <sub>25</sub> <b>C-H bend + CNC bend</b>		<b>9</b>	<b>759</b>	
v <sub>26</sub> <b>C-H bend + CCC bend</b>		<b>28</b>	<b>788</b>	<b>807</b>
v <sub>27</sub> <b>CCC bend + CNC bend</b>		<b>245</b>	<b>854</b>	<b>819</b>
v <sub>28</sub> CCC bend + CNC bend + C-H bend		2	861	
v <sub>29</sub> CCC bend		2	904	
v <sub>30</sub> CCC bend		2	906	
v <sub>31</sub> CCC bend + CH2 wag		8	926	
v <sub>32</sub> <b>C-H bend + CH2 wag</b>		<b>4</b>	<b>956</b>	<b>956</b>
v <sub>33</sub> C-H bend		21	961	
v <sub>34</sub> CCC bend + C-H bend + CH2 wag		85	963	
v <sub>35</sub> NCC bend + C-H bend		10	985	
v <sub>36</sub> C-H bend + CH2 wag + CNC bend + CCC bend		18	993	
v <sub>37</sub> C-H bend		1	1023	
v <sub>38</sub> C-H bend		68	1024	
v <sub>39</sub> C-H bend + CH2 wag + CCC bend		1	1041	
v <sub>40</sub> C-H bend + CH2 wag + CCC bend		58	1139	
v <sub>41</sub> C-H bend + NCC bend		1	1157	
v <sub>52</sub> C-H bend + C-N stretch		666	1473	
v <sub>53</sub> C-H bend + C-N stretch		5	1475	
v <sub>54</sub> <b>CH2 scissor + C=C stretch (bridge)</b>		<b>317</b>	<b>1478</b>	<b>1534</b>
v <sub>55</sub> CH2 scissor		11	1481	
v <sub>56</sub> C=N stretch + C-C aromatic stretch (ring) + C=C stretch (bridge)		<b>5025</b>	<b>1536</b>	<b>1603</b>
v <sub>57</sub> C=N stretch + C-C aromatic stretch (ring)		<b>441</b>	<b>1608</b>	<b>1641</b>
v <sub>58</sub> C=N stretch + C=C stretch (ring, bridge)		91	1630	
v <sub>59</sub> C=N stretch + C=C stretch (ring)		62	1684	
v <sub>60</sub> C=N stretch + C=C stretch (ring)		1	1689	
v <sub>61</sub> C=O stretch		10	1765	
v <sub>62</sub> C=O stretch		114	1769	

Cartesian coordinates, total energies, and vibrational zero-point energies for the optimized geometry from the B3LYP/6-31G\* calculations for the 3, 3'-dinitroazobenzene, didehydrozepine dimer formed, 3-hydroxy substituted didehydrozepine dimers and its corresponding ketone dimer, and 3-methoxy substituted didehydrozepine dimers.

### 3, 3'-dinitroazobenzene

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.734636	-2.197054	-0.000128
2	6	0	-1.877906	-1.087746	-0.000266
3	6	0	-2.409094	0.210576	-0.000111
4	6	0	-3.787879	0.353146	0.000176
5	6	0	-4.660027	-0.739036	0.000323
6	6	0	-4.118655	-2.022244	0.000165
7	7	0	-0.490205	-1.385217	-0.000627
8	7	0	0.262071	-0.375901	-0.000656
9	6	0	1.649642	-0.672622	-0.000330
10	6	0	2.192688	-1.970395	-0.000135
11	6	0	3.572426	-2.145588	0.000115
12	6	0	4.428937	-1.041186	0.000174
13	6	0	3.870198	0.234653	-0.000026
14	6	0	2.494785	0.441099	-0.000275
15	7	0	4.765612	1.406079	0.000028
16	8	0	5.977432	1.194608	0.000309
17	7	0	-4.359421	1.715262	0.000325
18	8	0	-5.585526	1.815489	0.000605
19	8	0	-3.576231	2.662168	0.000191
20	8	0	4.245621	2.519896	-0.000089
21	1	0	-1.758641	1.075120	-0.000232
22	1	0	-5.729063	-0.566844	0.000544
23	1	0	-4.776830	-2.885331	0.000266
24	1	0	-2.291137	-3.187740	-0.000266
25	1	0	2.081212	1.441668	-0.000436
26	1	0	5.506172	-1.152247	0.000360
27	1	0	3.991772	-3.147121	0.000257
28	1	0	1.516875	-2.817969	-0.000203

SCF Done: E(RB+HF-LYP) = -981.760513009      A.U. after 19 cycles  
Zero-point correction= 0.196180 (Hartree/Particle)

Didehydrozepine dimer:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.497845	1.553195	0.030521
2	6	0	-3.550128	0.731607	0.626436
3	6	0	-3.653739	-0.614565	0.534750
4	6	0	-2.713486	-1.515870	-0.100812
5	6	0	-1.431877	-1.249034	-0.454519
6	6	0	-0.694313	0.004598	-0.339536
7	6	0	0.694306	-0.004557	-0.339527
8	6	0	1.431878	1.249048	-0.454420
9	6	0	2.713516	1.515874	-0.100776
10	6	0	3.653805	0.614547	0.534665
11	6	0	3.550139	-0.731624	0.626408
12	6	0	2.497787	-1.553198	0.030585
13	7	0	1.313006	-1.261028	-0.370633
14	7	0	-1.313052	1.261015	-0.370658
15	1	0	-3.072598	-2.528668	-0.270572
16	1	0	-2.772950	2.605447	-0.096534
17	1	0	-4.357511	1.286352	1.100072
18	1	0	-4.547258	-1.078699	0.950587
19	1	0	-0.844707	-2.063391	-0.870390
20	1	0	2.772889	-2.605455	-0.096466
21	1	0	4.357538	-1.286394	1.099984
22	1	0	4.547393	1.078645	0.950393
23	1	0	3.072593	2.528687	-0.270520
24	1	0	0.844678	2.063444	-0.870174

SCF Done: E(RB+HF-LYP) = -572.691834882 A.U. after 16 cycles

Zero-point correction= 0.190263 (Hartree/Particle)

3-hydroxy substituted didehydrozepine dimer  
 Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.033650	-2.133775	0.093191
2	6	0	3.291471	-1.600605	0.622687
3	6	0	3.731772	-0.329942	0.534480
4	6	0	3.016483	0.789640	-0.061419
5	8	0	3.859039	1.860151	-0.251626
6	7	0	0.945616	-1.549960	-0.259272
7	6	0	0.674425	-0.179151	-0.252350
8	6	0	1.699159	0.851598	-0.372429
9	6	0	-0.671254	0.171637	-0.262797
10	6	0	-1.696834	-0.853296	-0.411095
11	6	0	-3.008652	-0.793979	-0.077357
12	8	0	-3.765151	-1.926444	-0.308044
13	7	0	-0.949596	1.544965	-0.300966
14	6	0	-2.030312	2.127754	0.073062
15	6	0	-3.257014	1.587517	0.662921
16	6	0	-3.689992	0.312570	0.578406
17	1	0	2.020589	-3.223607	-0.005970
18	1	0	3.950232	-2.340707	1.072016
19	1	0	4.722316	-0.083658	0.909938
20	1	0	1.317602	1.800918	-0.745880
21	1	0	-2.035729	3.215141	-0.052331
22	1	0	-3.892672	2.316209	1.161485
23	1	0	-4.652074	0.070484	1.032777
24	1	0	-1.350673	-1.794992	-0.826111
25	1	0	-4.704589	-1.691294	-0.292701
26	1	0	3.344340	2.597007	-0.617987

SCF Done: E(RB+HF-LYP) = -723.120590866      A.U. after 18 cycles  
 Zero-point correction= 0.197734 (Hartree/Particle)

3-methoxy substituted didehydrozepine dimer  
 Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.995760	2.243740	0.695669
2	8	0	-4.245499	0.949651	0.172707
3	6	0	-3.185338	0.096454	-0.001233
4	6	0	-1.901351	0.416070	0.298711
5	6	0	-0.701806	-0.406546	0.164006
6	6	0	0.548851	0.199662	0.128469
7	6	0	1.756926	-0.606360	0.243648
8	6	0	3.019016	-0.301000	-0.143290
9	8	0	3.993597	-1.273443	0.023002
10	6	0	5.004106	-0.947994	0.972464
11	7	0	-0.698563	-1.802552	0.199962
12	6	0	-1.655536	-2.592371	-0.130636
13	6	0	-2.991348	-2.316682	-0.660202
14	6	0	-3.664122	-1.151631	-0.585467
15	7	0	0.563803	1.603197	0.150665
16	6	0	1.494171	2.370685	-0.288810
17	6	0	2.771725	2.064462	-0.935361
18	6	0	3.452840	0.902799	-0.836791
19	1	0	-1.433007	-3.657170	-0.011071
20	1	0	-3.498998	-3.173665	-1.097960
21	1	0	-4.684479	-1.105019	-0.959064
22	1	0	-1.687721	1.414692	0.661527
23	1	0	1.300355	3.441590	-0.167652
24	1	0	3.229373	2.891219	-1.474571
25	1	0	4.428942	0.829058	-1.313612
26	1	0	1.612948	-1.594349	0.670691
27	1	0	-4.968132	2.737103	0.747925
28	1	0	-3.554904	2.191848	1.699719
29	1	0	-3.326563	2.817649	0.041311
30	1	0	5.717230	-1.775743	0.963855
31	1	0	5.530401	-0.018338	0.711963
32	1	0	4.578846	-0.840778	1.979815

SCF Done: E(RB+HF-LYP) = -801.733616162      A.U. after 18 cycles  
 Zero-point correction= 0.255204 (Hartree/Particle)

Ketone dimer

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.060015	1.967352	-0.295139
2	6	0	-2.964687	1.335855	0.664562
3	6	0	-3.080356	0.034654	1.021458
4	6	0	-2.422326	-1.122115	0.377391
5	8	0	-2.458395	-2.225718	0.899441
6	7	0	-1.007755	1.498153	-0.881687
7	6	0	-0.670577	0.163960	-0.898767
8	6	0	-1.749262	-0.888274	-0.974868
9	6	0	0.670614	-0.164169	-0.898705
10	6	0	1.749211	0.888133	-0.974918
11	6	0	2.422076	1.122159	0.377364
12	8	0	2.457846	2.225736	0.899431
13	7	0	1.008002	-1.498282	-0.881505
14	6	0	2.060329	-1.967343	-0.294999
15	6	0	2.964936	-1.335691	0.664679
16	6	0	3.080396	-0.034434	1.021441
17	1	0	-2.238710	3.032878	-0.451733
18	1	0	-3.576686	2.053663	1.209189
19	1	0	-3.733927	-0.232840	1.848393
20	1	0	-2.515505	-0.541174	-1.683120
21	1	0	2.239073	-3.032882	-0.451467
22	1	0	3.577015	-2.053357	1.209395
23	1	0	3.733929	0.233246	1.848350
24	1	0	2.515517	0.540919	-1.683070
25	1	0	1.335806	1.837021	-1.315893
26	1	0	-1.335887	-1.837230	-1.315676

E(RB+HF-LYP) = -723.163487440 A.U. after 16 cycles

Zero-point correction= 0.199592 (Hartree/Particle)