Insights into the Electronic Properties of Coumarins: A Comparative Study

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**Table S1:** **Bond length (in Å) of the different coumarins**

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Bond** | **C-1** |  | **C-2** | |  | **C-3** | |  | **C-4** | |  | **C-5** | |  | **C-6** | |  | **C-7** | |
| **BL** |  | **A** | **BL** |  | **A** | **BL** |  | **A** | **BL** |  | **A** | **BL** |  | **A** | **BL** |  | **A** | **BL** |
| O1-C2 | 1.474 |  | O1-C2 | 1.438 |  | O1-C2 | 1.435 |  | O1-C2 | 1.429 |  | O1-C2 | 1.437 |  | O1-C2 | 1.436 |  | O1-C2 | 1.426 |
| O1-C9 | 1.409 |  | O1-C9 | 1.376 |  | O1-C9 | 1.376 |  | O1-C9 | 1.386 |  | O1-C9 | 1.442 |  | O1-C9 | 1.316 |  | O1-C9 | 1.395 |
| C2-C3 | 1.496 |  | C2-C3 | 1.447 |  | C2-C3 | 1.450 |  | C2-C3 | 1.438 |  | C2-C3 | 1.536 |  | C2-C3 | 1.450 |  | C2-C3 | 1.442 |
| C3-H12 | 1.097 |  | C3-H12 | 1.081 |  | C3-H12 | 1.081 |  | C3-H12 | 1.080 |  | C3-H12 | 1.070 |  | C3-H12 | 1.081 |  | C3-H12 | 1.079 |
| C3-C4 | 1.364 |  | C3-C4 | 1.360 |  | C3-C4 | 1.356 |  | C3-C4 | 1.365 |  | C3-C4 | 1.343 |  | C3-C4 | 1.358 |  | C3-C4 | 1.362 |
| C4-C10 | 1.476 |  | C4-C10 | 1.448 |  | C4-C10 | 1.452 |  | C4-C10 | 1.459 |  | C4-C10 | 1.532 |  | C4-C10 | 1.448 |  | C4-C10 | 1.455 |
| C5-C10 | 1.423 |  | C5-C10 | 1.409 |  | C5-C10 | 1.404 |  | C5-C10 | 1.423 |  | C5-C10 | 1.401 |  | C5-C10 | 1.414 |  | C5-C10 | 1.404 |
| C5-C6 | 1.396 |  | C5-C6 | 1.380 |  | C5-C6 | 1.387 |  | C5-C6 | 1.396 |  | C5-C6 | 1.400 |  | C5-C6 | 1.398 |  | C5-C6 | 1.390 |
| C6-C7 | 1.430 |  | C6-C7 | 1.420 |  | C6-C7 | 1.406 |  | C6-C7 | 1.404 |  | C6-C7 | 1.400 |  | C6-C7 | 1.416 |  | C6-C7 | 1.399 |
| C7-C8 | 1.413 |  | C7-C8 | 1.404 |  | C7-C8 | 1.396 |  | C7-C8 | 1.390 |  | C7-C8 | 1.401 |  | C7-C8 | 1.382 |  | C7-C8 | 1.416 |
| C8-C9 | 1.419 |  | C8-C9 | 1.388 |  | C8-C9 | 1.388 |  | C8-C9 | 1.388 |  | C8-C9 | 1.402 |  | C8-C9 | 1.396 |  | C8-C9 | 1.400 |
| C9-C10 | 1.437 |  | C9-C10 | 1.412 |  | C9-C10 | 1.414 |  | C9-C10 | 1.418 |  | C9-C10 | 1.406 |  | C9-C10 | 1.408 |  | C9-C10 | 1.416 |
| C2-O11 | 1.252 |  | C2-O11 | 1.221 |  | C2-O11 | 1.220 |  | C2-O11 | 1.228 |  | C2-O11 | 1.258 |  | C2-O11 | 1.220 |  | C2-O11 | 1.229 |
| C4-C13 | 1.537 |  | C4-C13 | 1.514 |  | C4-C13 | 1.513 |  | C4-C13 | 1.508 |  | C4-C13 | 1.540 |  | C4-C13 | 1.514 |  | C4-C13 | 1.507 |
| C13-H14 | 1.099 |  | C13-H14 | 1.092 |  | C13-H14 | 1.092 |  | C13-H14 | 1.089 |  | C13-H14 | 1.070 |  | C13-H14 | 1.092 |  | C13-H14 | 1.092 |
| C13-H15 | 1.102 |  | C13-H15 | 1.096 |  | C13-H15 | 1.096 |  | C13-H15 | 1.089 |  | C13-H15 | 1.070 |  | C13-H15 | 1.092 |  | C13-H15 | 1.088 |
| C13-H16 | 1.102 |  | C13-H16 | 1.096 |  | C13-H16 | 1.096 |  | C13-H16 | 1.089 |  | C13-H16 | 1.070 |  | C13-H16 | 1.096 |  | C13-H16 | 1.092 |
| C5-H17 | 1.098 |  | C5-H17 | 1.082 |  | C5-H17 | 1.082 |  | C5-O17 | 1.389 |  | C5-H17 | 1.070 |  | C5-H17 | 1.083 |  | C5-H17 | 1.079 |
| C6-H18 | 1.098 |  | C6-H18 | 1.083 |  | C6-H18 | 1.080 |  | O17-C18 | 1.465 |  | C6-O18 | 1.430 |  | C6-O17 | 1.398 |  | C6-H18 | 1.078 |
| C7-O19 | 1.410 |  | C7-N19 | 1.369 |  | C7-O19 | 1.378 |  | C18-H19 | 1.090 |  | O18-C19 | 1.430 |  | O17-H18 | 0.988 |  | C7-O19 | 1.381 |
| O19-H20 | 1.026 |  | N19-H20 | 1.011 |  | O19-C18 | 1.462 |  | C18-H20 | 1.090 |  | C18-H20 | 1.070 |  | C7-O19 | 1.372 |  | O19-C20 | 1.464 |
| C8-H21 | 1.096 |  | N19-H21 | 1.012 |  | C18-H20 | 1.089 |  | C18-C21 | 1.516 |  | C18-H21 | 1.070 |  | O19-H20 | 0.998 |  | C20-H21 | 1.094 |
| - | - |  | C8-H22 | 1.082 |  | C18-H21 | 1.096 |  | C21-H22 | 1.089 |  | C18-C22 | 1.540 |  | C8-H22 | 1.079 |  | C20-H22 | 1.094 |
| - | - |  | - | - |  | C18-H22 | 1.096 |  | C21-H23 | 1.089 |  | C22-H23 | 1.070 |  | - | - |  | C20-C23 | 1.516 |
| - | - |  | - | - |  | C18-H22 | 1.079 |  | C21-H24 | 1.092 |  | C22-H24 | 1.070 |  | - | - |  | C23-H24 | 1.092 |
| - | - |  | - | - |  | - | - |  | C6-H25 | 1.075 |  | C22-H25 | 1.070 |  | - | - |  | C23-H25 | 1.089 |
| - | - |  | - | - |  | - | - |  | C7-O26 | 1.386 |  | C7-O26 | 1.430 |  | - | - |  | C23-H26 | 1.092 |
| - | - |  | - | - |  | - | - |  | O26-C27 | 1.453 |  | O26-C27 | 1.430 |  | - | - |  | C8-O27 | 1.376 |
| - | - |  | - | - |  | - | - |  | C27-H28 | 1.092 |  | C27-H28 | 1.070 |  | - | - |  | O27-C28 | 1.481 |
| - | - |  | - | - |  | - | - |  | C26-H29 | 1.092 |  | C27-H29 | 1.070 |  | - | - |  | C28-H29 | 1.088 |
| - | - |  | - | - |  | - | - |  | C26-C30 | 1.516 |  | C27-C30 | 1.540 |  | - | - |  | C28-H30 | 1.088 |
| - | - |  | - | - |  | - | - |  | C30-H31 | 1.089 |  | C30-H31 | 1.070 |  | - | - |  | C28-C31 | 1.516 |
| - | - |  | - | - |  | - | - |  | C30-H32 | 1.089 |  | C30-H32 | 1.070 |  | - | - |  | C31-H32 | 1.090 |
| - | - |  | - | - |  | - | - |  | C30-H33 | 1.092 |  | C30-H22 | 1.070 |  | - | - |  | C31-H33 | 1.090 |
| - | - |  | - | - |  | - | - |  | C8-H34 | 1.077 |  | C8-H34 | 1.077 |  | - | - |  | C31-H34 | 1.092 |

**Table S2: Bond angles of coumarins C-1 to C-3**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Bond** | **C-1** |  | **C-2** | |  | **C-3** | |
| **BA (º)** |  | **A** | **BA (º)** |  | **A** | **BA (º)** |
| O1-C2-C3 | 117.13 |  | O1-C2-C3 | 114.82 |  | O1-C2-C3 | 114.91 |
| O1-C2-O11 | 115.63 |  | O1-C2-O11 | 117.00 |  | O1-C2-O11 | 117.26 |
| C2-C3-C4 | 123.71 |  | C2-C3-C4 | 123.71 |  | C2-C3-C4 | 123.84 |
| C2-C3-H12 | 114.95 |  | C2-C3-H12 | 115.04 |  | C2-C3-H12 | 114.89 |
| C3-C4-C13 | 121.16 |  | C3-C4-C13 | 120.51 |  | C3-C4-C13 | 120.74 |
| C3-C4-C10 | 118.78 |  | C3-C4-C10 | 119.74 |  | C3-C4-C10 | 119.54 |
| C4-C13-H14 | 110.23 |  | C4-C13-H14 | 110.53 |  | C4-C13-H14 | 110.53 |
| C5-C6-C7 | 119.85 |  | C5-C6-C7 | 120.78 |  | C5-C6-C7 | 119.86 |
| C5-C6-H18 | 120.55 |  | C5-C6-H18 | 120.04 |  | C5-C6-H18 | 119.46 |
| C7-C8-H21 | 120.46 |  | C7-C8-C21 | 121.14 |  | C7-C8-C24 | 119.77 |
| C7-O19-H20 | 103.22 |  | C7-N19-H20 | 120.91 |  | C7-O19-C20 | 118.53 |
| C8-C9-C10 | 120.95 |  | C8-C9-C10 | 121.45 |  | C8-C9-C10 | 121.04 |
| C9-C8-H21 | 119.85 |  | C9-C8-H22 | 118.07 |  | C9-C8-H24 | 119.96 |

**Table S3: Bond angles of coumarins C-4 to C-5**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **C-4** | | **C-** | **C-5** | |  | **C-6** | |  | **C-7** | |
| **A** | **BA** |  | **A** | **BA** |  | **A** | **BA** |  | **A** | **BA** |
| O1-C2-C3 | 114.98 |  | O1-C2-C3 | 121.19 |  | O1-C2-C3 | 114.66 |  | O1-C2-C3 | 115.50 |
| O1-C2-O11 | 117.29 |  | O1-C2-O11 | 119.39 |  | O1-C2-O11 | 117.32 |  | O1-C2-O11 | 117.10 |
| C2-C3-C4 | 124.44 |  | C2-C3-C4 | 119.21 |  | C2-C3-C4 | 123.86 |  | C2-C3-C4 | 123.34 |
| C2-C3-H12 | 114.95 |  | C2-C3-H12 | 120.40 |  | C2-C3-H12 | 114.95 |  | C2-C3-H12 | 115.22 |
| C3-C4-C13 | 118.25 |  | C3-C4-C13 | 120.71 |  | C3-C4-C13 | 120.62 |  | C3-C4-C13 | 120.34 |
| C3-C4-C10 | 119.04 |  | C3-C4-C10 | 118.56 |  | C3-C4-C10 | 119.60 |  | C3-C4-C10 | 119.88 |
| C4-C13-H14 | 109.94 |  | C4-C13-H14 | 109.47 |  | C4-C13-H14 | 110.51 |  | C4-C13-H14 | 110.84 |
| C5-C6-C7 | 119.71 |  | C5-C6-C7 | 119.92 |  | C5-C6-C7 | 120.78 |  | C5-C6-C7 | 120.56 |
| C5-C6-H25 | 120.12 |  | C5-C6-O18 | 120.04 |  | C5-C6-O18 | 126.79 |  | C5-C6-H18 | 119.42 |
| C7-C8-C34 | 121.02 |  | C6-O18-C19 | 109.47 |  | C6-O18-H19 | 111.75 |  | C7-O19-C20 | 119.72 |
| C5-O17-C18 | 120.24 |  | O18-C19-H20 | 109.47 |  | C7-C8-C22 | 120.24 |  | O19-C20-H21 | 109.38 |
| O17-C18-H19 | 109.16 |  | C7-O26-C27 | 109.47 |  | C7-O19-H20 | 106.77 |  | C20-O23-H24 | 110.46 |
| C18-C21-H22 | 110.78 |  | O26-C27-H28 | 109.47 |  | C8-C9-C10 | 121.06 |  | C8-O27-C28 | 125.02 |
| C7-O25-C26 | 119.79 |  | C27-C30-H31 | 119.85 |  | C9-C8-H24 | 119.82 |  | O27-C28-H29 | 109.36 |
| O25-C26-H27 | 111.22 |  | C8-C9-C10 | 119.36 |  | - | - |  | C28-C31-H32 | 109.88 |
| C26-C29-H30 | 112.26 |  | C9-C8-H34 | 119.86 |  | - | - |  | C8-C9-C10 | 122.42 |
| C8-C9-C10 | 123.62 |  | - | - |  | - | - |  | C9-C8-O27 | 127.51 |
| C9-C8-H34 | 120.38 |  | - | - |  | - | - |  | - | - |

**Table S4: Theoretical calculated excitation energy, and other solvation energies of C-7**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Molecule** | **C-7** | | | |
| **Parameters** | **gaseous** | **benzene** | **ethanol** | **water** |
| Eext (eV) | 4.012 | 4.084 | 3.776 | 3.789 |
| ECav (Kcal/mol) | – | 28.92 | 26.41 | 36.69 |
| EDisper (Kcal/mol) | – | -20.36 | -18.82 | -21.34 |
| ERepul (Kcal/mol) | – | 1.44 | 0.82 | 0.98 |
| Enon-el (Kcal/mol) | – | 10.00 | 8.42 | 16.33 |
| EPSS(Kcal/mol) | – | -4.72 | -13.06 | -14.69 |
| Gsol (Kcal/mol) | – | 5.28 | -5.47 | 0.66 |

**Table S5: Theoretical dipole moment of coumarins in gaseous phase and other solvent medium (benzene, ethanol and water).**

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Medium** | **C-1** |  | **C-2** |  | **C-3** |  | **C-4** |  | **C-5** |  | **C-6** |  | **C-7** |
| Gaseous | 7.357 |  | 7.146 |  | 7.436 |  | 6.233 |  | 7.863 |  | 7.971 |  | 5.899 |
| Benzene | 8.034 |  | 7.705 |  | 7.826 |  | 8.094 |  | 8.958 |  | 8.554 |  | 7.487 |
| Ethanol | 9.595 |  | 9.153 |  | 10.637 |  | 12.785 |  | 10.372 |  | 10.386 |  | 8.968 |
| Water | 9.770 |  | 9.300 |  | 10.315 |  | 13.149 |  | 10.554 |  | 10.511 |  | 9.182 |