Supplementary materials

Theoretical Study of Structure and Photophysics of Homologous Series of Bis(arylydene)cycloalkanones

Roman Starostin, Alexandra Freidzon, S.P. Gromov

Table S1 Comparison of experimental and calculated chemical shifts

|  |
| --- |
| Cyclobutanones |
| **Proton** **group** | 4-H | 4-OMe | 3,4-OMe |
| Calculation | Experiment | Calculation | Experiment | Calculation | Experiment |
| 4H (С(3)Н2) | 3.93 | 3.89 | 3.80 | 3.78 | 3.77 | 3.81 |
| 2H (methine) | 7.36 | 7.19 | 7.23 | 7.11 | 7.20 | 7.10 |
| Cyclopentanones |
| **Proton** **group** | 4-H | 4-OMe | 3,4-OMe |
| Calculation | Experiment | Calculation | Experiment | Calculation | Experiment |
| 4H (С(3-4)Н2) | 3.25 | 3.12 | 3.06 | 3.08 | 3.05 | 3.08 |
| 2H (methine) | 7.86 | 7.6 | 7.67 | 7.56 | 7.66 | 7.51 |
| Cyclopentanones |
| **Proton** **group** | 4-H | 4-OMe | 3,4-OMe |
| Calculation | Experiment | Calculation | Experiment | Calculation | Experiment |
| 4H (С(3,5)Н2) | 3.05 | 2.96 | 3.00 | 2.94 | 3.11 | 2.95  |
| 4H (С(4)Н2) | 1.69 | 1.80 | 1.70 | 1.80 | 1.75 | 1.81 |
| 2H (methine) | 8.38 | 7.72 | 8.28 | 7.67 | 8.27 | 7.66 |

|  |  |
| --- | --- |
|  |  |

Figure S1 Calculated and experimental chemical shifts in 4-H (solid), 4-OMe (dashed), and 3,4-OMe (dotted).

|  |
| --- |
| Cyclobutanone |
|  |  |
| Cyclopentanone |
|  |  |
| Cyclohexanone |
|  |  |

Figure S2 Correlations between the calculated HOMO and LUMO energies and experimental oxidation and reduction potentials.

|  |
| --- |
| Cyclobutanone |
|  |
| Cyclopentanone |
|  |
| Cyclohexanone |
|  |

Figure S3. Correlations between the calculated HOMO-LUMO gap and experimental gap between the oxidation and reduction potentials.

|  |  |
| --- | --- |
|  |  |
| **a** | **b** |

Figure S4. Oscillator strengths of the first and second ππ\* transitions.



**(a)**



**(b)**

****

**(c)**

Figure S5. Energy diagrams of the excited states of (E,E) isomer in cyclobutanone (a), cyclopentanone (b) and cyclopentanone (c) series.

Table S2 Experimental and calculated electronic transitions

|  |
| --- |
| Cyclobutanones |
|  | **λabs, nm** | **λfl, nm** |
| **Dienone** | **Experiment**  | **Calculation (Osc. Strength)** | **type** | **Experiment**  | **Calculation (τrad, ns)** | **type** |
| **1a** | 356 | 359 (0.90)378 (2·10-7) | π–π\*n–π\* | - | 411 (2.3·107) | n–π\* |
| **1b** | 385 | 393 (1.10) | π–π\* | - | 419 (2.28) | π–π\* |
| **1c** | 401 | 427 (0.83) | π–π\* | 505 | 446 (3.48) | π–π\* |
| **1d** | 402 | 432 (1.11) | π–π\* | 522 | 452 (2.62) | π–π\* |
| **1e** | 481 | 471 (1.23) | π–π\* | 575 | 491 (2.86) | π–π\* |
| Cyclopentanones |
|  | **λabs, nm** | **λfl, nm** |
| **Dienone** | **Experiment**  | **Calculation (Osc. Strength)** | **type** | **Experiment**  | **Calculation (τrad, ns)** | **type** |
| **2a** | 347 | 371 (1.16)379 (6.5·10-5) | π–π\*n–π\* | - | 401 (1.0·107) | n–π\* |
| **2b** | 380 | 395 (1.36) | π–π\* | - | 422 (1.8) | π–π\* |
| **2c** | 395 | 420 (1.22) | π–π\* | 500 | 439 (2.2) | π–π\* |
| **2d** | 396 | 424 (1.42) | π–π\* | 508 | 458 (2.0) | π–π\* |
| **2e** | 471 | 472 (1.79) | π–π\* | 562 | 482 (1.9) | π–π\* |
| Cyclohexanones |
|  | **λabs, nm** | **λfl, nm** |
| **Dienone** | **Experiment**  | **Calculation (Osc. Strength)** | **type** | **Experiment**  | **Calculation (τrad, ns)** | **type** |
| **3a** | 326 | 348 (0.92)375 (0.07) | π–π\*n–π\* | - | 414 (778) | n–π\* |
| **3b** | 356 | 385 (1.02) | π–π\* | - | 431 (2.90) | π–π\* |
| **3c** | 370 | 404 (1.04) | π–π\* | - | 432 (2.26) | π–π\* |
| **3d** | 368 | 410 (1.21) | π–π\* | - | 441 (2.02) | π–π\* |
| **3e** | 445 | 455 (1.54) | π–π\* | 562 | 495 (2.46) | π–π\* |