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**Figure S1** Intramolecular hydrogen bonds (dotted line) in the two ***E*** and *Z*-**4e-c** geometricalisomers of enaminoesters.

**Table S1**. The values of ρ, ∇2ρ and Hamiltonian -H(r) for *E*-**4b** isomer calculated at the BCP

|  |  |  |  |
| --- | --- | --- | --- |
| ***E*-4e** | Gas phase | Polar solvent (ε=3.75) | Non polar solvent (ε=0.19) |
| ρ×10³ | ▽²ρ×10³  | -H(r)×10⁴  | ρ×10³ | ▽²ρ×10³  | -H(r)×10⁴  | ρ×10³ | ▽²ρ×10³  | -H(r)×10⁴  |
| 1 | 21.38 | 74.73 | 4.72 | 23.18 | 81.79 | 8.06 | 22.31 | 78.32 | 6.37 |
| 2 | 10.60 | 42.55 | 16.65 | 10.35 | 43.42 | 19.38 | 10.59 | 42.41 | 16.45 |
| 3 | 13.93 | 59.09 | 14.33 | 14.33 | 60.47 | 14.23 | 14.00 | 59.37 | 14.34 |
| 4 | 6.32 | 20.89 | 9.00 | 6.67 | 21.69 | 9.17 | 6.40 | 21.00 | 8.97 |

**Table S2**. The values of ρ, ∇2ρ and Hamiltonian -H(r) for *Z*-**4b** isomer calculated at the BCP

|  |  |  |  |
| --- | --- | --- | --- |
| ***Z*-4e** | Gas phase | Polar solvent (ε=3.75) | Non polar solvent (ε=0.19) |
| ρ×10³ | ▽²ρ×10³  | H(r)×10⁴  | ρ×10³ | ▽²ρ×10³  | H(r)×10⁴  | ρ×10³ | ▽²ρ×10³  | H(r)×10⁴  |
| 1 | 12.08 | 50.38 | 14.20 | 11.25 | 46.97 | 14.18 | 11.83 | 49.23 | 13.90 |
| 2 | 11.78 | 47.71 | 11.75 | 11.72 | 48.18 | 12.70 | 11.94 | 48.26 | 11.76 |
| 3 | 6.89 | 25.79 | 8.33 | 5.78 | 22.17 | 7.77 | 6.52 | 24.57 | 8.22 |
| 4 |  |  |   | 10.77 | 41.93 | 7.54 |  |  |  |
| 5 |   |   |   | 11.72 | 48.18 | 12.70 | 14.71 | 73.52 | 28.47 |

**Table S3**. The values of ρ, ∇2ρ and Hamiltonian -H(r) for ***E***-**4c** isomer calculated at the BCP

|  |  |  |  |
| --- | --- | --- | --- |
| **E-4c** | Gas phase | Polar solvent (ε=3.75) | Non polar solvent (ε=0.19) |
| ρ×10³ | ▽²ρ×10³ | -H(r)×10⁴ | ρ×10³ | ▽²ρ×10³ | -H(r)×10⁴ | ρ×10³ | ▽²ρ×10³ | -H(r)×10⁴ |
| 1 | 22.09 | 77.35 | 5.70 | 22.10 | 77.33 | 5.46 | 22.38 | 78.48 | 6.11 |
| 2 | 15.55 | 72.46 | 24.84 | - | - | - | 15.48 | 72.64 | 25.22 |
| 3 | 14.05 | 52.96 | 9.63 | 13.81 | 51.75 | 9.37 | 14.00 | 52.67 | 9.54 |
| 4 | 10.62 | 42.49 | 16.28 | 10.37 | 46.83 | 23.54 | 10.50 | 42.70 | 17.38 |
| 5 | 13.68 | 67.25 | 31.16 | 13.73 | 67.69 | 31.39 | 13.70 | 67.39 | 31.22 |
| 6 | 6.58 | 22.00 | 9.49 | 6.89 | 23.05 | 9.94 | 6.66 | 22.19 | 9.53 |
| 7 | 13.92 | 59.12 | 14.36 | 14.33 | 60.42 | 14.20 | 14.05 | 59.53 | 14.31 |
| 8 | - | - | - | 13.22 | 48.86 | 9.66 | 13.31 | 49.15 | 9.62 |

**Table S4** The values of ρ, ∇2ρ and Hamiltonian -H(r) for ***Z***-**4c** isomer calculated at the BCP

|  |  |  |  |
| --- | --- | --- | --- |
| **Z-4c** | Gas phase | Polar solvent (ε=3.75) | Non polar solvent (ε=0.19) |
| ρ×10³ | ▽²ρ×10³  | -H(r)×10⁴  | ρ×10³ | ▽²ρ×10³  | -H(r)×10⁴  | ρ×10³ | ▽²ρ×10³  | -H(r)×10⁴  |
| 1 | 10.6 | 40.4 | 6.85 | 6.10 | 28.90 | 13.52 | 9.63 | 38.07 | 8.42 |
| 2 | 17.29 | 72.81 | 18.4 | 17.19 | 74.48 | 20.57 | 17.27 | 72.98 | 18.69 |
| 3 | 13.75 | 50.65 | 8.69 | 13.48 | 49.35 | 8.49 | 13.64 | 50.21 | 8.66 |
| 4 | 11.44 | 47.42 | 17.08 | 11.20 | 48.88 | 20.35 | 11.40 | 47.56 | 17.49 |
| 5 | 13.81 | 67.62 | 31.17 | 13.90 | 68.20 | 31.40 | 13.83 | 67.77 | 31.24 |
| 6 | 3.38 | 13.53 | 6.37 | - | - | - | 3.32 | 13.38 | 6.33 |
| 7 | 11.98 | 50.13 | 15.37 | 11.30 | 47.23 | 14.77 | 11.87 | 49.65 | 15.25 |
| 8 |   |   |   | 5.58 | 22.29 | 9.08 |   |   |   |

**Table S5.** The most important geometrical parameters corresponding to H Bonds (Bond Lengths) and bonding angles for the two isomers of **4e.**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| ***E*-4e** | Gas phase | Solvent ε=3.75 | solvent ε=0.19 | ***Z*-4e** | Gas phase | Solvent ε=3.75 | solvent ε=0.19 |
| O29 H33…O35 | 1.96a(163.55)b | 1.92 (168.23) | 1.94 (165.84) | C1 H3…O35 | 2.57 (93.04) | 2.59 (94.83) | 2.58 (93.19) |
| C31 H32…O35 | 2.53 (119.02) | 2.56 (101.85) | 2.53 (119.33) | C31 H32…O44 | 2.43 (114.79) | 2.44 (113.68) | 2.43 (114.79) |
| C45 O44…C34 | 2.64 (148.09) | 2.63 (146.56) | 2.64 (131.49) | C17 C16…O29 | 3.17 (106.03) | 3.24 (107.04) | 3.19 (106.67) |
| C15 H30…C1 | 2.90 (115.10) | 2.89 (114.65) | 2.90 (114.68) | C31N15…O35 |  | 2.96 (116.14) |  |
|  |  |  |  | C31H32…O29 |  | 2.33 (103.85) | 2.33 (103.67) |

a *Bond lengths are in angstroms*

b *bonding angles*

**Table S6** The most important geometrical parameters corresponding to H Bonds (Bond Lengths) and bonding angles for the two isomers of **4c.**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| ***E*-4c** | Gas phase | Solvent ε=3.75 | solvent ε=0.19 | ***Z*-4c** | Gas phase | Solvent ε=3.75 | solvent ε=0.19 |
| O42 H46…O48 | 1.95a (165.08)b | 1.94 (164.98) | 1.94 (165.45) | O42 H46…O55 | 2.34 (137.99) | 2.64 (123.25) | 2.39 (135.79) |
| C44 H45…O42 | 2.34 (107.32) | 2.35 (107.05) | 2.34 (107.25) | C44 H45…O42 | 2.31 (106.86) | 2.31 (105.26) | 2.31 (106.65) |
| C34 H36…O42 | 2.33 (118.19) | 2.35 (118.06) | 2.34 (118.13) | C34 H36…O42 | 2.37 (118.85) | 2.38 (118.75) | 2.37 (118.79) |
| C44 H45…O48 | 2.53 (165.08) | 2.58 (117.20) | 2.54 (118.56) | C26 H29…O42 | 2.48 (113.81) | 2.51 (113.25) | 2.49 (113.74) |
| C23 H24…C30 | 2.42 (102.46) | 2.42 (102.50) | 2.42 (102.48) | C23 H24…O30 | 2.42 (102.52) | 2.41 (102.58) | 2.41(102.54) |
| C19 H43…C1 | 2.86(115.92) | 2.83(116.78) | 2.86(115.98) | C19H43…O48 | 3.46 (85.45) |  | 3.51 (83.81) |
| O48 C47…O56 | 2.64(100.91) | 2.63( 98.92) |  | C1 H3…O48 | 2.55 (94.79) | 2.58 (95.59) | 2.56 (94.91) |
| C26H29…O42 |   | 2.40(116.43) | 2.39(116.39) | C44H45…O57 |   | 2.53 (112.96) |   |

a *Bond lengths are in angstroms*

b *bonding angles*