**Electronic Supplementary information (ESI)**

**Intramolecular hydrogen bonds of gossypol imine derivatives**

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**Computational benchmark test**

We performed a benchmark test for five different gossypol imine derivatives (Schiff bases and hydrazones with aliphatic and aromatic substituents). Thus, we optimized the geometries of five selected compounds (**1**, **3**, **8**, **15**, **19**) using the B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) methods in the gas phase.

In Table S1, S2, S3, S4 and S5 collected calculated geometric characteristics using the B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) methods and EHB(rH) values of compounds **1**, **3**, **8**, **15**, **19**.

**Table S1**. Calculated Hydrogen bond length (rH(O∙∙∙H), Å) and EHB(rH) of C(6)O–H∙∙∙OC(7) of compounds **1**, **3**, **8**, **15**, **19**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | rH(O∙∙∙H), Å | | EHB(rH), kcal/mol | |
| **I** | **II** | **I** | **II** |
| **1**  (dienamine) | 1.894 | 1.912 | 7.0 | 6.6 |
| **3**  (dienamine) | 1.888 | 1.906 | 7.2 | 6.8 |
| **8**  (dienamine) | 1.881 | 1.900 | 7.4 | 6.9 |
| **15**  (diimine) | 1.963 | 1.976 | 5.6 | 5.4 |
| **19**  (diimine) | 1.953 | 1.968 | 5.8 | 5.5 |

**I** – B3LYP/6-311G(d,p) method;

**II** – B3LYP/6-311++G(d,p) method.

**Table S2**. Calculated Hydrogen bond length (rH(O∙∙∙H), Å) and EHB(rH) of N(13)–H∙∙∙OC(7) of compounds **1**, **3**, **8**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | rH(O∙∙∙H), Å | | EHB(rH), kcal/mol | |
| **I** | **II** | **I** | **II** |
| **1**  (dienamine) | 1.724 | 1.724 | 12.3 | 12.3 |
| **3**  (dienamine) | 1.726 | 1.724 | 12.2 | 12.3 |
| **8**  (dienamine) | 1.756 | 1.756 | 11.1 | 11.1 |

**I** – B3LYP/6-311G(d,p) method;

**II** – B3LYP/6-311++G(d,p) method.

**Table S3**. Calculated Hydrogen bond length (rH(O∙∙∙H), Å) and EHB(rH) of C(7)O–H∙∙∙N(13) of compounds **15** and **19**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | rH(N∙∙∙H), Å | | EHB(rH), kcal/mol | |
| **I** | **II** | **I** | **II** |
| **15**  (diimine) | 1.658 | 1.654 | 15.2 | 15.4 |
| **19**  (diimine) | 1.616 | 1.614 | 17.4 | 17.6 |

**I** – B3LYP/6-311G(d,p) method;

**II** – B3LYP/6-311++G(d,p) method.

**Table S4**. Calculated Hydrogen bond length (rH(O∙∙∙H), Å) and EHB(rH) of C(11)–H∙∙∙O of compounds **1**, **3**, **8**, **15**, **19**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | rH(O∙∙∙H), Å | | EHB(rH), kcal/mol | |
| **I** | **II** | **I** | **II** |
| **1**  (dienamine) | 1.982 | 1.981 | 5.3 | 5.3 |
| **3**  (dienamine) | 1.986 | 1.992 | 5.2 | 5.1 |
| **8**  (dienamine) | 1.986 | 1.984 | 5.2 | 5.3 |
| **15**  (diimine) | 1.991 | 1.986 | 5.1 | 5.2 |
| **19**  (diimine) | 1.983 | 1.983 | 5.3 | 5.3 |

**I** – B3LYP/6-311G(d,p) method;

**II** – B3LYP/6-311++G(d,p) method.

**Table S5**. Calculated Hydrogen bond length (rH(O∙∙∙H), Å) and EHB(rH) of С(1)О–Н∙∙∙π of compounds **1**, **3**, **8**, **15**, **19**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Compound | rH(O∙∙∙H), Å | | EHB(rH), kcal/mol | |
| **I** | **II** | **I** | **II** |
| **1**  (dienamine) | 2.162 | 2.167 | 2.9 | 2.9 |
| **3**  (dienamine) | 2.161 | 2.169 | 3.0 | 2.9 |
| **8**  (dienamine) | 2.161 | 2.165 | 3.0 | 2.9 |
| **15**  (diimine) | 2.140 | 2.150 | 3.2 | 3.1 |
| **19**  (diimine) | 2.145 | 2.153 | 3.1 | 3.0 |

**I** – B3LYP/6-311G(d,p) method;

**II** – B3LYP/6-311++G(d,p) method.

Comparison of Wall clock times for performing calculations by B3LYP/6-311G(d,p) method, B3LYP/6-311G(d,p) method with adding diffuse functions to the basis sets of atoms involved in the hydrogen bonds formation and B3LYP/6-311++G(d,p) method.

**Table S6**. Wall clock times in percents for performing the entire SCF and 2-electron gradient of compounds **1**, **3**, **8**, **15**, **19**.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | SCF time, % | | | 2-electron gradient time, % | | |
|  | **I** | **II** | **III** | **I** | **II** | **III** |
| **1**  (dienamine) | 100 | 104 | 577 | 100 | 108 | 194 |
| **3**  (dienamine) | 100 | 104 | 674 | 100 | 107 | 193 |
| **8**  (dienamine) | 100 | 106 | 611 | 100 | 107 | 185 |
| **15**  (diimine) | 100 | 105 | 644 | 100 | 108 | 185 |
| **19**  (diimine) | 100 | 107 | 577 | 100 | 110 | 182 |

100 % time for B3LYP/6-311G(d,p) method;

**I** – B3LYP/6-311G(d,p) method;

**II** – B3LYP/6-311G(d,p) method with adding diffuse functions to the basis sets of atoms involved in the hydrogen bonds formation;

**III** – B3LYP/6-311++G(d,p) method.

**Correlation plots**

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**Fig. S1.** Correlations between EHB(rH) and EHB(α, R) values of C(6)O–H∙∙∙OC(7) (a) and C(7)O–H∙∙∙N(13) (b) intramolecular hydrogen bonds ((a) EHB(rH)=2.07EHB(α, R)+4.67; r=0.986; SD=0.14; n=21; (b) EHB(rH)=2.25EHB(α, R)+2.99; r=0.994; SD=0.32; n=7).