Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science


# The Effect of Dimerization on the Excited State Behavior of Methylated Xanthine Derivatives: A Computational Study

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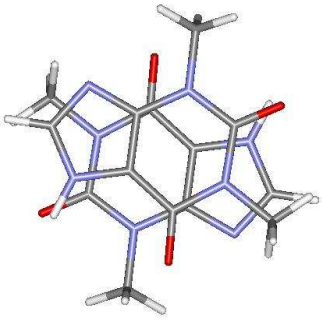
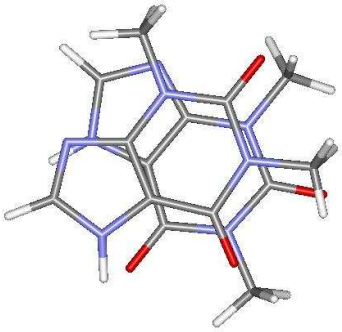
## Supplementary Material



*1,3-diMet-X-S1*



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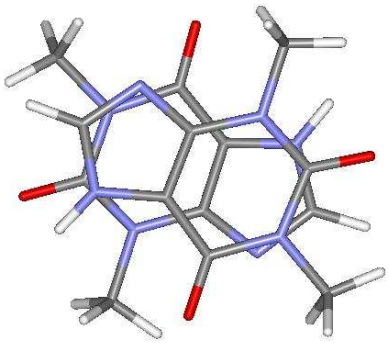
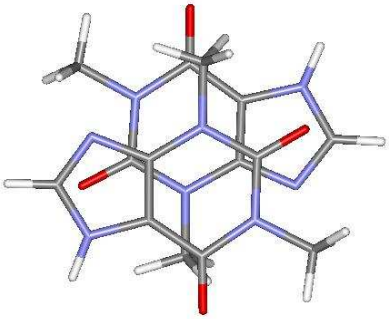
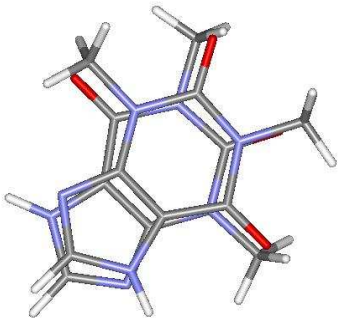


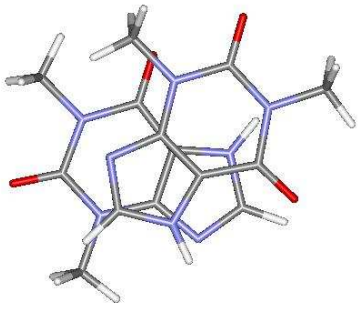
*1,3-diMet-X-S3*



*1,3-diMet-X-S4*

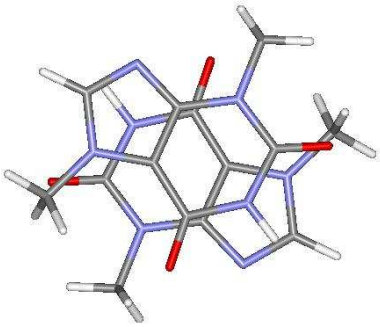


*1,3-diMet-X-S5*

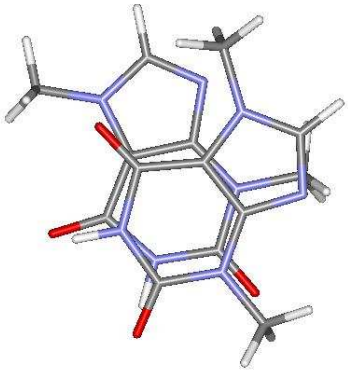


*1,3-di-Met-X-6*

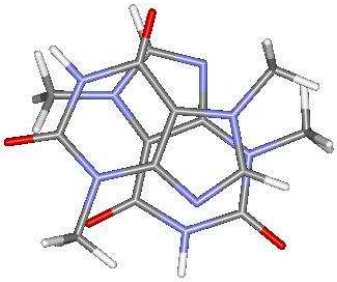
SI – 1. The ground state equilibrium structures of the most stable complexes of *1,3-diMet-X* optimized at the B97D/TZVP level. The C, N, O and H atoms are colored in grey, blue, red and white, respectively.



*3,7-diMet-X-S1*



*3,7-diMet-X-S2*



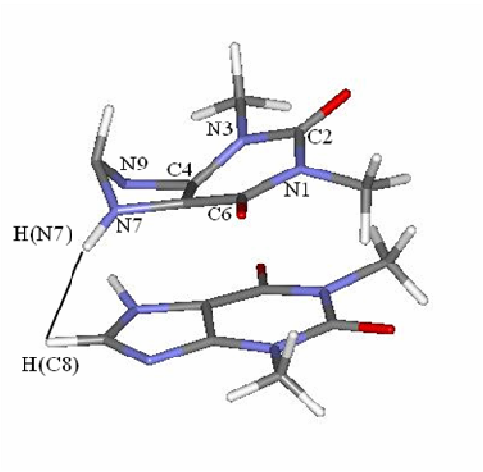
*3,7-diMet-X-S3*

SI-2. The ground state equilibrium structures o the most stable complexes of *3,7-diMet-X* optimized at the B97D/TZVP level. The C, N,O and H atoms are colored in grey, blue, red and white, respectively.

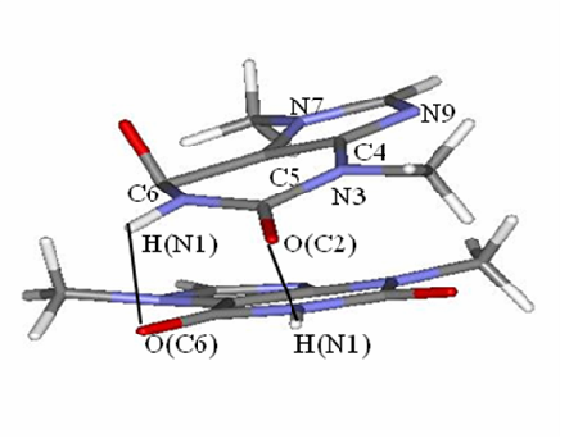
| | | delta E (eV)[b] | Electronic configuration of excitation | % | Electronic configuration of excitation | % |
|---|---|---|---|---|---|---|
| *1,3-diMet-X-S1* | $S_1$ | 4.670 | HOMO→LUMO+1 | 58.5 | HOMO-1→LUMO | 31.4 |
| | $S_2$ | 4.769 | HOMO→LUMO | 63.1 | HOMO-1→LUMO+1 | 24.8 |
| *1,3-diMet-X-S2* | $S_1$ | 4.645 | HOMO→LUMO | 69.2 | HOMO-1→LUMO | 16.5 |
| | $S_2$ | 4.866 | HOMO→LUMO+1 | 56.1 | HOMO-1→LUMO+1 | 24.3 |
| *1,3-diMet-X-S3* | $S_1$ | 4.687 | HOMO→LUMO+1 | 33.6 | HOMO-1→LUMO | 32.0 |
| | $S_2$ | 4.772 | HOMO→LUMO | 44.1 | HOMO-1→LUMO | 18.7 |
| *1,3-diMet-X-S4* | $S_1$ | 4.569 | HOMO→LUMO | 75.0 | | |
| | $S_2$ | 4.795 | HOMO→LUMO+1 | 57.7 | HOMO-1→LUMO | 29.3 |
| *1,3-diMet-X-S5* | $S_1$ | 4.618 | HOMO→LUMO+1 | 42.1 | HOMO-1→LUMO | 40.6 |
| | $S_2$ | 4.660 | HOMO→LUMO | 48.6 | | |
| *1,3-diMet-X-S6* | $S_1$ | 4.551 | HOMO→LUMO | 67.9 | | |
| | $S_2$ | 4.756 | HOMO→LUMO+1 | 43.7 | HOMO-1→LUMO | 32.3 |
| *3,7-diMet-X-S1* | $S_1$ | 4.651 | HOMO→LUMO+1 | 49.2 | HOMO-1→LUMO | 26.5 |
| | $S_2$ | 4.790 | HOMO→LUMO | 48.1 | HOMO-1→LUMO+1 | 26.4 |
| *3,7-diMet-X-S2* | $S_1$ | 4.636 | HOMO→LUMO+1 | 63.4 | HOMO-1→LUMO | 26.1 |
| | $S_2$ | 4.769 | HOMO→LUMO | 60.2 | HOMO-1→LUMO+1 | 27.4 |
| *3,7-diMet-X-S3* | $S_1$ | 4.674 | HOMO→LUMO | 49.8 | HOMO-1→LUMO | 34.5 |
| | $S_2$ | 4.788 | HOMO→LUMO+1 | 47.9 | HOMO-1→LUMO+1 | 35.4 |
| *1,3,7-triMet-X-S1* | $S_1$ | 4.531 | HOMO→LUMO+1 | 66.2 | HOMO-1→LUMO | 22.7 |
| | $S_2$ | 4.688 | HOMO→LUMO | 60.1 | HOMO-1→LUMO+1 | 26.1 |
| *1,3,7-triMet-X-S2* | $S_1$ | 4.595 | HOMO→LUMO | 45.3 | HOMO-1→LUMO | 30.9 |
| | $S_2$ | 4.688 | HOMO→LUMO+1 | 40.4 | HOMO-1→LUMO+1 | 20.4 |
| *1,3,7-triMet-X-S3* | $S_1$ | 4.633 | HOMO→LUMO | 62.4 | HOMO-1→LUMO+1 | 24.8 |
| | $S_2$ | 4.684 | HOMO→LUMO+1 | 61.2 | HOMO-1→LUMO | 23.5 |
| *1,3,7-triMet-X-S4* | $S_1$ | 4.633 | HOMO→LUMO | 61.2 | HOMO-1→LUMO+1 | 24.1 |
| | $S_2$ | 4.733 | HOMO-1→LUMO+1 | 58.5 | HOMO-1→LUMO | 23.9 |

SI-3. Character of the wavefunctions of the two lowest excited states of dimers in Franck-Condon region.

*1,3-diMet-X-S5-oop-imid*




*3,7-diMet-X-S2-oopO*




| Dihedral angle (°) | *1,3-diMet-oop-imid* (monomer) | *1,3-diMet-X-S5-oop-imid* |
|---|---|---|
| N1-C2-N3-C4 | -0.2 | 2.1 |
| C2-N3-C4-C5 | -3.3 | 3.6 |
| N3-C4-C5-C6 | 5.3 | -4.9 |
| N9-C4-C5-C6 | -165.9 | -175.0 |
| C8-N9-C4-C5 | 11.9 | 19.73 |
| C8-C4-N3-C2 | 107.5 | 107.2 |
| Distance (Å) | | |
| H(N7)-H(C8) | | 2.17 |

| | *3,7-diMet-oopO* (monomer) | *3,7-diMet-X-S2-oopO* |
|---|---|---|
| Dihedral angle (°) | | |
| N3-C2-N1-C6 | -1.7 | -27.5 |
| C4-N3-C2-N1 | -12.3 | -3.2 |
| C5-C4-N3-C2 | 1.3 | 7.3 |
| C8-N7-C4-C5 | 0.2 | -1.0 |
| O(C2)-C2-N3-C4 | 172.7 | 161.3 |
| O(C6)-C6-N1-C2 | -60.7 | -82.5 |
| C6-N1-C2-N3 | -27.4 | -179.0 |
| Distance (Å) | | |
| H(N1)-O(C6) | | 2.64 |
| O(C2)-H(N1) | | 2.61 |

SI-4. Comparison of structure parameters of *oopO* and *oopimid* conical intersections for monomer and dimer.

*1,3,7-triMet-X-S3-deloc*

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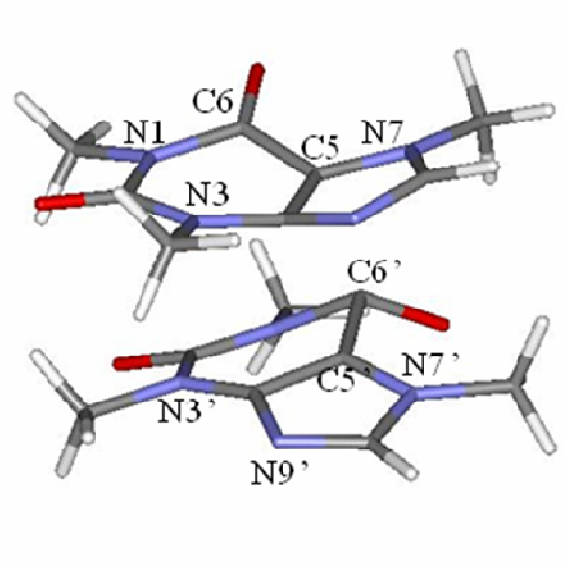
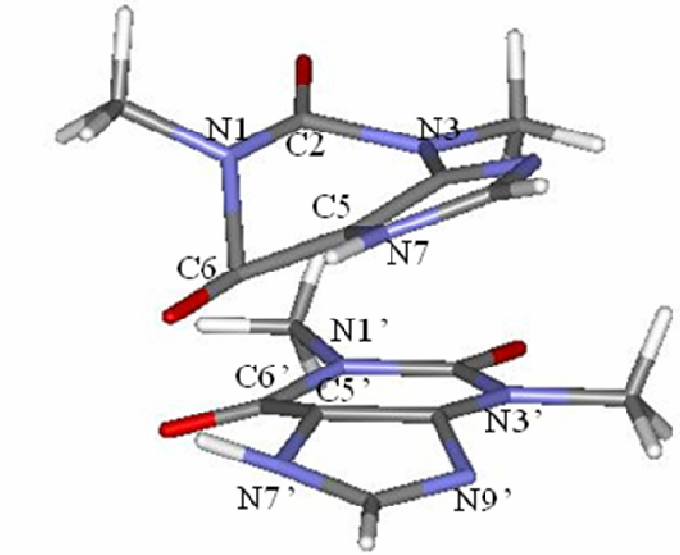
| Distances (in Å) | |
|---|---|
| N1-C2’ | 3.19 |
| C5-C6’ | 2.32 |
| N3-C4’ | 2.87 |
| Dihedral angles (°) | |
| C6-N1-C2-N3 | -11.0 |
| N9-C4-N3-C2 | -160.9 |
| N7-C5-C6-N1 | -156.3 |
| C8-N7-C4-C5 | -1.7 |
| N1’-C2’-N3’-C4’ | -9.9 |
| C5’-C4’-N3’-C2’ | 13.2 |
| N3’-C4’-C5’-C6’ | 8.8 |
| N7’-C5’-C6’-N1’ | 144.5 |




*1,3-diMet-X-S2-deloc*

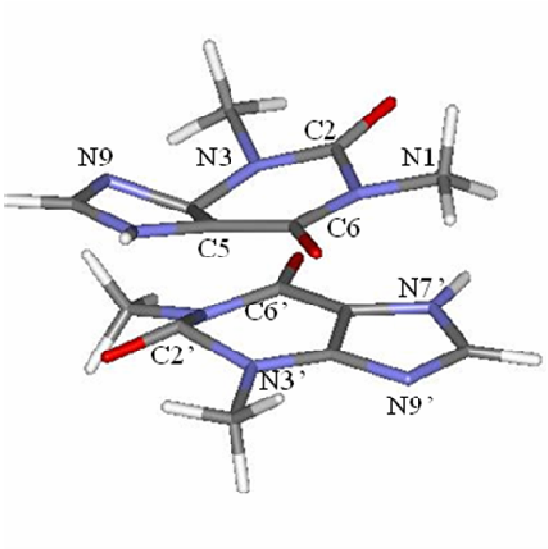
| Distances (in Å) | |
|---|---|
| N3-C2’ | 3.01 |
| C6-C5’ | 1.96 |
| C5-C4’ | 2.96 |
| Dihedral angles | |
| N1-C2-N3-C4 | 14.2 |
| N7-C5-C4-N9 | 8.9 |
| C6-N1-C2-N3 | -35.8 |
| N7-C5-C6-N9 | 131.9 |
| C6’-N1’-C2’-N3’ | -11.8 |
| C5’-C4’-N3’-C2’ | 0.8 |
| N7’-C5’-C6’-N1’ | -167.0 |
| N9’-C4’-N3’-C2’ | -157.2 |




SI-5. Illustrative structure parameters for delocalized conical intersections.

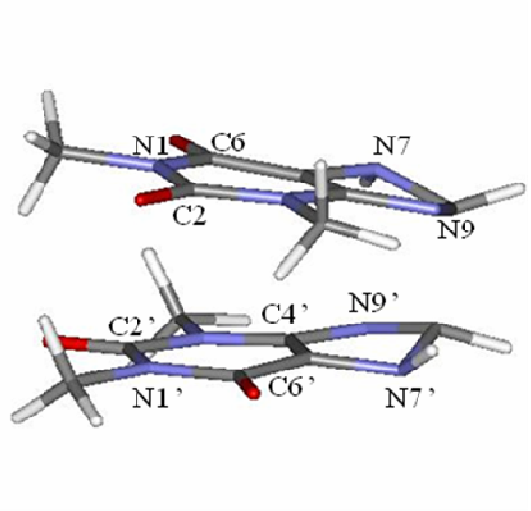
*1,3-diMet-X-S1-bond*

| Distance (Å) | |
|---|---|
| N1-C4’ | 2.82 |
| C4-C2’ | 1.90 |
| Dihedral angle (°) | |
| N1-C2-N3-C4 | 15.2 |
| C2-N1-C6-C5 | 13.7 |
| N9-C4-N3-C2 | 137.2 |
| N7-C8-N9-C4 | 10.5 |
| C6’-N1’-C2’-N3’ | -42.5 |
| N7’-C8’-N9’-C4’ | 1.6 |
| N3’-C4’-C5’-C6’ | -10.3 |
| N1’-C2’-N3’-C4’ | 28.4 |



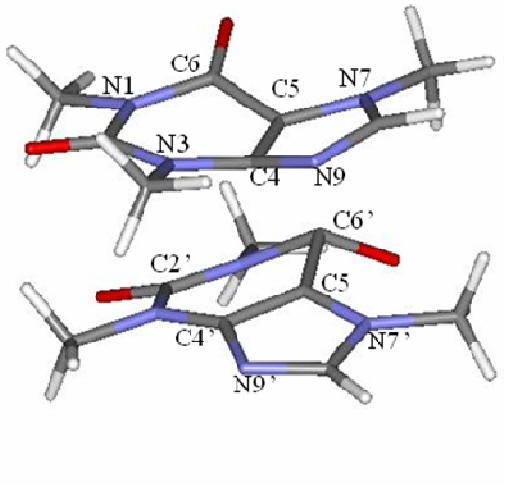

*1,3-diMet-X-S5-bond*

| Distance (Å) | |
|---|---|
| N1-N1’ | 3.11 |
| C8-C8’ | 1.95 |
| Dihedral angle (°) | |
| N1-C2-N3-C4 | -6.0 |
| N3-C4-C5-C6 | 3.6 |
| C5-N7-C8-N9 | -22.7 |
| C6-C5-N7-C8 | -170.0 |
| C6’-C5’-N7’-C8’ | -171.8 |
| C5’-N7’-C8’-N9’ | -25.8 |
| N1’-C2’-N3’-C4’ | -4.5 |




*1,3,7-triMet-X-S3-bond*

| Distance (Å) | |
|---|---|
| N1-C6 | 3.08 |
| C4-C4’ | 1.97 |
| Dihedral angle (°) | |
| N1-C2-N3-C4 | -17.9 |
| C2-N3-C4-C5 | 29.9 |
| N9-C4-N3-C2 | 155.0 |
| N7-C8-N9-C4 | 5.4 |
| N9’-C4’-N3’-C2’ | -153.3 |
| N7’-C8’-N9’-C4’ | -5.6 |
| N1’-C2’-N3’-C4’ | 1.9 |




SI-6. Illustrative structure parameters for *bond* conical intersections.