Comparative computational study of electronic excitations of neutral and charged small oligothiophenes and their extrapolations based on simple models

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All neutral molecules of OTₙ have nonplanar ground state structures, as is well known, whereas charged molecules have planar ones. There is significant variation in the C=C−C=C dihedral angles among different methods. Table S1 provides values for the dihedral angles calculated by different methods, and Table S2 provides bond distances for the structures optimized for the first excited state. Schematic of OT₆ and labeling convention are provided in Fig. S1.

![Figure S1. Schematics of OT₆ and labeling convention. Some of obvious labels are omitted. For example, the carbon next to carbon 5 in the same thiophene ring is 6 and that next to 8 is 7.](image)

**Table S1. Dihedral angles for the optimized structures in the ground electronic state calculated by PM6, and DFT calculations with 6-31+G (d,p) basis set in both vacuum (v) and solution phase (s). The solution phase is for PCM model of CHCl₃.** For each n, the first row is the dihedral angle formed by carbon atoms (3, 4, 5, 6) in Fig. 5. The next ones, where applicable, are for (7,8,9,10), (11,12,13,14), (15,16,17,18), and (19,20,21,22).

| n | PM6 | B3LYP | BVP86 | M06-2X |
|---|-----|-------|-------|--------|
| 2 | 2v  | 141   | 156   | 158    | 0      |
|   | sv  | 140   | 158   | 160    | 0      |
| 3 | 3v  | 142   | 159   | 163    | -157   |
|   | 3s  | 142   | -159  | -163   | 153    |
| 4 | 4v  | 160   | 166   | 155    | 155    |
|   | 4s  | 160   | 166   | -166   | 173    |
| 5 | 5v  | 145   | 156   | 157    | 157    |
|   | 5s  | 145   | 156   | -156   | 173    |
| 6 | 6v  | 147   | 162   | 166    | 156    |
|   | 6s  | 147   | 162   | 166    | 156    |


Table S2. Bond distances between rings (in Å) for S₁ state of OTₙ. For each n, from the top to the last raw applicable, the data represent bond distances between carbon atoms labeled (4,5), (8,9), (12,13), (16,17), and (20,21). The TD-DFT method was used employing the basis of 6-31+G(d,p) for all the calculations in both vacuum (v) and solution phases calculated at the PCM level, where sᵃ is for acetonitrile and sᵇ is for dioxane.

| n  | B3LYP   | BVP86   | M06-2X  |
|----|---------|---------|---------|
| 4  | v       | 1.41953 | 1.42491 | 1.41919 |
|    |         | 1.40386 | 1.41881 | 1.39385 |
|    |         | 1.41953 | 1.42490 | 1.41921 |
|    | sᵃ      | 1.41399 | 1.41950 | 1.41457 |
|    |         | 1.39384 | 1.40787 | 1.38448 |
|    |         | 1.41401 | 1.41952 | 1.41450 |
|    | sᵇ      | 1.41693 | 1.42238 | 1.41691 |
|    |         | 1.39946 | 1.41370 | 1.38978 |
|    |         | 1.41694 | 1.42239 | 1.41693 |
| 5  | v       | 1.42696 | 1.44649 | 1.43052 |
|    |         | 1.40944 | 1.44169 | 1.40221 |
|    |         | 1.40944 | 1.44002 | 1.40224 |
|    |         | 1.42696 | 1.44649 | 1.43054 |
|    | sᵃ      | 1.42384 | 1.42606 | 1.42860 |
|    |         | 1.40013 | 1.41231 | 1.39373 |
|    |         | 1.40013 | 1.41230 | 1.39379 |
|    |         | 1.42384 | 1.42606 | 1.42861 |
|    | sᵇ      | 1.42541 | 1.42760 | 1.42939 |
|    |         | 1.40526 | 1.41775 | 1.39846 |
|    |         | 1.40525 | 1.41775 | 1.39850 |
|    |         | 1.42541 | 1.42760 | 1.42944 |
| 6  | v       | 1.43190 | 1.43145 | 1.43796 |
|    |         | 1.41490 | 1.42443 | 1.41253 |
|    |         | 1.40972 | 1.42569 | 1.40076 |
|    |         | 1.41490 | 1.42443 | 1.41253 |
|    |         | 1.43189 | 1.43145 | 1.43774 |
|    | sᵃ      | 1.43116 | 1.43069 | 1.43796 |
|    |         | 1.41167 | 1.41653 | 1.40696 |
|    |         | 1.40505 | 1.41337 | 1.39084 |
|    |         | 1.41167 | 1.41653 | 1.40696 |
|    |         | 1.43116 | 1.43069 | 1.43796 |
|    | sᵇ      | 1.43073 | 1.43853 | 1.43754 |
|    |         | 1.40787 | 1.42906 | 1.40990 |
|    |         | 1.39927 | 1.42878 | 1.39647 |
|    |         | 1.40787 | 1.42935 | 1.40992 |
|    |         | 1.43073 | 1.43856 | 1.43754 |

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