# A density functional study of the ground and excited state potential energy surfaces of a light-driven rotary molecular motor (3R,3'R)-(P,P)-trans-1,1',2,2',3,3',4,4'-octahydro-3,3'-dimethyl-4,4'-biphenanthrylidene.

## Supporting information.

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Table 1: The geometry parameters of the (3R,3'R)-(P,P)-trans-1,1',2,2',3,3',4,4'-octahydro-3,3'-dimethyl-4,4'-biphenanthrylidene molecular motor (see scheme 1 for the labels) in the four conformations: (P,P)-*trans*-**1**, (M,M)-*cis*-**2**, (P,P)-*cis*-**2**, (M,M)-*trans*-**1** (denoted in the table as PPT, MMC, PPC, MMT, correspondingly), optimized with B3LYP using two different basis sets and the relative B3LYP ground state energies with respect to PP-trans conformation in eV. The experimental values [1] are shown in brackets

| | 6-31G*/STO-3G | | | | 6-31G* | | | |
|---|---|---|---|---|---|---|---|---|
| | PPT | MMC | PPC | MMT | PPT | MMC | PPC | MMT |
| $\alpha$ | 186.6 | -17.8 | 2.2 (-3.2) | 160.1 | 188.6 | -17.6 | 0.9 (-3.2) | 161.1 |
| $\alpha'$ | -165.6 | -21.2 | 5.4 (5.9) | 151.7 | -164.0 | -22.7 | 7.2 (5.9) | 150.8 |
| $\beta$ | 67.1 | -46.1 | 54.1 (54.4) | -44.0 | 68.6 | -48.2 | 56.1 (54.4) | -45.1 |
| $\gamma$ | -121.8 | -41.8 | -94.3 (-97.0) | -44.8 | -118.9 | -40.3 | -95.1 (-97.0) | -44.1 |
| $\gamma'$ | -121.8 | -41.8 | -94.3 (-96.0) | -44.8 | -118.9 | -40.3 | -95.1 (-96.0) | -44.1 |
| $\zeta$ | 190.5 | 178.3 | 181.6 | 175.8 | 192.3 | 177.4 | 183.1 | 174.8 |
| $\varphi$ | 124.3 | 120.7 | 124.4 | 122.1 | 123.7 | 120.9 | 124.9 | 122.1 |
| 1 | 1.356 | 1.377 | 1.362 (1.347) | 1.378 | 1.357 | 1.377 | 1.361 (1.347) | 1.378 |
| 2 | 1.495 | 1.500 | 1.494 | 1.495 | 1.494 | 1.498 | 1.493 | 1.492 |
| 3 | 1.399 | 1.402 | 1.400 | 1.406 | 1.393 | 1.396 | 1.394 | 1.399 |
| 4 | 1.523 | 1.520 | 1.523 | 1.520 | 1.509 | 1.506 | 1.509 | 1.506 |
| 5 | 1.569 | 1.558 | 1.562 | 1.558 | 1.544 | 1.535 | 1.538 | 1.535 |
| 6 | 1.580 | 1.562 | 1.569 | 1.556 | 1.570 | 1.551 | 1.558 | 1.545 |
| 7 | 1.532 | 1.559 | 1.541 | 1.563 | 1.532 | 1.557 | 1.540 | 1.559 |
| $\Delta E$ | 0.00 | 0.56 | -0.01 | 0.45 | 0.00 | 0.62 | 0.03 | 0.43 |

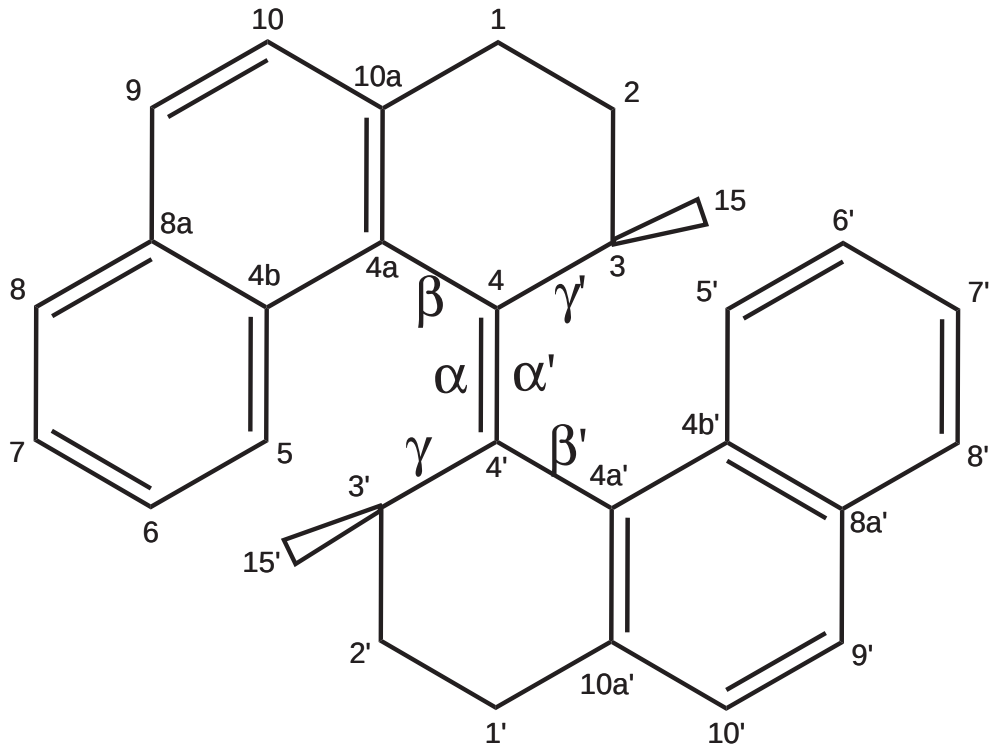
Table 2: The vertical excitation energies in the (P,P)-*trans*-**1** and (P,P)-*cis*-**2** conformations. The geometries optimized with two different basis sets[a] were used. The excitation energies were calculated with the use of TD-BH&HLYP and SA-REBH&HLYP and three different basis sets[b]. Deviations from the experimental data are shown. All energies are in eV.

| | SA-REKS | | | | TDDFT | | | |
|---|---|---|---|---|---|---|---|---|
| | A | | B | | A | | B | |
| (P,P)-*trans*-**1** | | | | | | | | |
| | $S_1$-$S_0$ | Error | $S_1$-$S_0$ | Error | $S_1$-$S_0$ | Error | $S_1$-$S_0$ | Error |
| 1 | 4.87 | 0.81 | 4.88 | 0.82 | 4.79 | 0.73 | 4.80 | 0.74 |
| 2 | 4.47 | 0.41 | 4.50 | 0.44 | 4.27 | 0.21 | 4.30 | 0.24 |
| 3 | 4.41 | 0.35 | 4.44 | 0.38 | 4.19 | 0.14 | 4.23 | 0.17 |
| Exp.[c] | 4.06 | | 4.06 | | 4.06 | | 4.06 | |
| (P,P)-*cis*-**2** | | | | | | | | |
| | $S_1$-$S_0$ | Error | $S_1$-$S_0$ | Error | $S_1$-$S_0$ | Error | $S_1$-$S_0$ | Error |
| 1 | 4.65 | 0.44 | 4.65 | 0.44 | 4.63 | 0.42 | 4.63 | 0.42 |
| 2 | 4.23 | 0.02 | 4.29 | 0.08 | 4.17 | -0.04 | 4.20 | -0.01 |
| 3 | 4.18 | -0.03 | 4.24 | 0.03 | 4.10 | -0.11 | 4.14 | -0.07 |
| Exp.[c] | 4.21 | | 4.21 | | 4.21 | | 4.21 | |

[a] A: REB3LYP/hybrid 6-31G*/STO-3G optimized structures; B: REB3LYP/6-31G* optimized structures.

[b] 1: hybrid 6-31G*/STO-3G; 2: 6-31G*; 3: 6-311G**

[c] Cited from Ref. [1].




α=(4a, 4, 4',4a'); α'=(3, 4, 4',3')
β=(4', 4, 4a,4b); β'=(4, 4', 4a',4b')
γ=(4, 4', 3',15'); γ'=(4', 4, 3,15)
ζ=(3, 4, 4',4a); φ=(3, 4, 4')
1=44'; 2=44a; 3=4a10a;
4=10a1; 5=12; 6=23; 7=34

Scheme 1:

# References

[1] Harada, N. ; Koumura, N.; Feringa, B. L. *J. Am. Chem. Soc.* **1997**, *119*, 7256.