

Supporting Material

Tunability in Polyatomic Molecule Diffusion through Tunneling versus Pacing

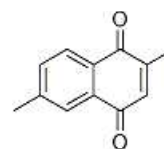
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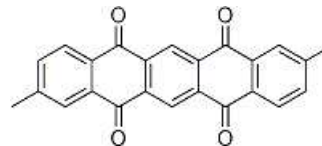
Synthesis

2,6-Dimethylnaphthaquinone is prepared as follows:¹ Periodic acid (10.11g, 44.4 mmol) is dissolved in 195 ml of acetonitrile, followed by the addition of chromium (VI) oxide (105.6 mg, 1.506 mmol). The resulting solution is cooled to 5 °C. 2,6-Dimethylnaphthalene (1.65 g, 10.56 mmol) is dissolved in 15 ml of acetonitrile and added all at once to the above solution with stirring. Solution turned pale yellow upon addition of 2,6-dimethylnaphthalene. After stirring for 1 h, the supernatant liquid of the reaction mixture is decanted into another flask and solvent is removed under reduced pressure. Remaining residue is dissolved in H₂O and CH₂Cl₂, and extracted using CH₂Cl₂ (30 ml x 2). Organic layer is washed with brine (30 ml) and H₂O (30 ml x 2) and then dried over anhydrous Mg₂SO₄. Solvent is removed under reduced pressure. Recovered 1.5638 g 2,6-dimethylnaphthaquinone (80.3% yield). Product is purified by sublimation. HRMS and NMR agree with reports in the literature.



2,9-Dimethylpentacene-5,7,12,14-tetrone is prepared as follows:²

2,6-dimethylnaphthaquinone (0.85 g, 4.56 mmol) is dissolved in 65 ml of ethanol. To this solution 1.3 ml of diethylamine is added



and allowed to stir overnight in the dark. Reaction mixture is filtered. Recovered 0.1248 g of 2,9-Dimethylpentacene-5,7,12,14-tetrone (16.4% yield). Product is recrystallized in *o*-dichlorobenzene. ¹H-NMR (300 MHz, CDCl₃): δ 2.588 (s, 6H), δ 7.68 (d, 2H), δ 8.20 (s, 2H), δ 8.29 (d, 2H), δ 9.23 (s, 2H). HRMS (*m/z*): [M]⁺ calculated for C₂₄H₁₄O₄, 366.0892; found, 366.0891.

Movies:

Movie 1: Frames at variable delay taken from series of STM images showing uniaxial diffusion of PQ, PT and DPT. Imaging parameters: PQ 2.2V, 90 pA, 41K; PT 2.7V, 130 pA, 40K; DPT 1.6V, 110 pA, 68K. All frames approx. 52 Å x 27 Å

Movie 2: Molecular configurations during trotting, pacing and gliding motion obtained from DFT-based optimization of molecular configurations as described in the manuscript. The hooves in the “horse” animation are placed according to the positions of the oxygen atoms obtained from DFT calculations.

References:

- ¹ S. Yamazaki, *Tetrahedron Letters* **42**, 3355 (2001).
- ² I. Baxter, D. W. Cameron, and R. B. Titman, *Journal of the Chemical Society C-Organic*, 1253 (1971).