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Preparation of 6,11-Dihydroxy-5,12-tetracenedione

Elisey Yagodkin, Kathryn A. McGarry, and Christopher J. Douglas

Department of Chemistry, University of Minnesota–Twin Cities, Minneapolis MN 55455, USA

Linear acene derivatives such as substituted anthracenes and tetracenes are well known for their properties as organic semiconductors and fluorophores. 1,6,11-Dihydroxy-5,12-tetracenedione (3) (Scheme 1) is an important and common substrate for the synthesis of tetracene derivatives with semiconducting properties and other organic electronic materials.2–8

\[
\text{Cl} \quad \text{OH} \\
\text{Cl} \quad \text{OH} \\
\text{PhNO}_2 \quad \text{AlCl}_3 \\
\text{OH} \quad \text{O} \\
\text{OH} \quad \text{O}
\]

Scheme 1

Our syntheses of tetracene derivatives necessitated access to inexpensive, analytically pure, multi-gram quantities of 3. A previous procedure for the preparation of 3 was reported by Sartori in 1987.9 In our hands, Sartori’s procedure was unwieldy at a larger scale because of difficult extractions and column chromatography. Moreover, we could only obtain 3 in significantly diminished yield and purity at the larger scale, compared to the original report. Older approaches for the synthesis of 3 involve rearrangements and condensations that proceed in low yields and also involve difficult purifications.10,11 Although 3 is commercially available, its high cost (Aldrich lists 1g for $63.20 at 96% purity, May 2010) makes it a significant financial barrier in academic research.

Our procedure makes substantial modifications to Sartori’s procedure, affording analytically pure 3 on a multi-gram scale using only washing and precipitation techniques. If one synthesizes 1,4-naphthalenediol (1), over 10 grams of 3 are produced using reagents and solvents costing a total of $57 (May 2010). Although 1 is also commercially available,
it is the most expensive precursor of 3. Therefore, we prepared 1 on large scale in analogy to Knapp’s original procedure. The high purity and large scale of our procedures allows the synthesis of organic materials for applications in field effect transistors and/or solar cells.

**Experimental Section**

All reagents and solvents were reagent grade and used without further purification unless otherwise specified. Although 1,4-naphthalenediol (1) can be purchased (TCI America, $106 for 25 g, May 2010), it is the most expensive reagent in the procedure. Therefore, we have provided the procedure for 1, at our scale, for reference. The material is identical by $^1$H NMR spectroscopy with the material purchased from TCI. Either the prepared material or the material purchased from TCI can be used to synthesize 3.

**1,4-Naphthalenediol (1)**

Water (600 mL) and diethyl ether (500 mL) were placed into a 2-L Erlenmeyer flask containing a large stir bar (5 cm). The flask was closed with a large two-holed stopper (size 12) and fitted with a nitrogen inlet and outlet (attached to a mineral oil bubbler). The mixture was degassed by bubbling nitrogen through for 20 min at 3–5 bubbles per second and the mixture was stirred gently. Sodium dithionite (80.0 g, 0.460 mol) and 1,4-naphthoquinone (15.8 g, 0.100 mol) were added. The mixture was stirred vigorously for 30 min under nitrogen. The biphasic mixture formed a heterogeneous suspension upon vigorous stirring. The aqueous phase was removed using a 2-L separatory funnel. All separatory-funnel operations were completed within 10 min; extended exposure to air led to decreases in yield and purity. The organic phase was washed with 500 mL of water, dried (Na$_2$SO$_4$, 20.0 g), filtered, and concentrated under reduced pressure to give 1,4-naphthalenediol as a light brown solid, 14.7 g (93%), mp 190–192°C (lit.$^{1,3}$ mp 193–194°C). Because 1,4-naphthalenediol is light and air sensitive, it was stored in brown-glass bottle and used within 48 h after preparation.

**6,11-Dihydroxy-5,12-tetracenedione (3)**

A flame-dried 500-mL 3-necked round-bottomed flask was fitted with an overhead mechanical stirrer, septum and glass adapter with a line to nitrogen gas. Under a nitrogen atmosphere, AlCl$_3$ (30.0 g, 0.220 mol, 3.5 equiv.) was placed in the flask as a solid. Nitrobenzene (25 mL, dried over CaH$_2$ and distilled before use) was added using a syringe and the mixture was stirred at 60°C (oil bath) for 30 min. Additional nitrobenzene was added until a fine light yellow suspension was obtained (approximately 15 mL). 1,4-Naphthalenediol (10.0 g, 0.062 mol, 1.0 equiv., added as a solid) and phthaloyl chloride (13.0 g, 0.064 mol, 1.0 equiv., distilled before use and added as a liquid via syringe) were added portion-wise over 5 min to the reaction flask, alternating portions of each reagent. Additional nitrobenzene (approximately 10 mL) was used to wash down the starting materials that adhered to the flask. The deep red reaction mixture was stirred for 4 h at 90°C (oil bath), allowed to cool to room temperature and the septum was replaced with an addition funnel. The addition funnel was charged with 12 M HCl (200 mL) that was added slowly over
20 min (Caution, gas evolution). The black reaction mixture was transferred to a 2-L Erlenmeyer flask equipped with a magnetic stir bar and additional 12 M HCl (350 mL) was used to wash the remaining contents from the 3-necked flask into the Erlenmeyer flask. The resulting mixture was stirred vigorously at room temperature for 1 h. The slurry is filtered through a 500 mL fine porosity fritted glass filter. [The filtration process was time consuming (overnight or a whole day) as the slurry slowly went through the fine fritted glass filter (4–5.5 microns). The use of a medium porosity filter (10–16 microns) gave poor mass recovery. Swirling and mixing the material on the filter with a spatula from time to time helped speed the filtration.] The resulting dark red solid was washed with acetone (200 mL) and dried overnight on the glass filter. The solid was transferred into a 2-L Erlenmeyer flask equipped with a magnetic stir bar using acetone (800 mL) and the resulting mixture was stirred vigorously at room temperature for 14 h. The slurry was filtered through a 500 mL fine porosity fritted glass filter and washed with acetone (200 mL), then dried overnight on the filter. The resulting solid was transferred into a 2 L Erlenmeyer flask equipped with a magnetic stir bar containing a solution of sodium potassium tartrate tetrahydrate (90.0 g, 0.300 mol) in H2O (1300 mL), and the mixture was stirred vigorously with a magnetic stirrer for 2 h at 70°C using a hot plate, and an additional 10 h at room temperature. The mixture was filtered though a 500 mL fine-porosity fritted glass filter, and the solid was washed sequentially with 12 M HCl (200 mL), warm (45–50°C) H2O (1000 mL) and acetone (500 mL). The resulting solid was dried for 14 h in a vacuum desiccator (vacuum measured to be 0.1 Torr which was then left as a static vacuum) over P2O5 (20 g) to give the final product as a red powder 12.0 g (67% yield), mp 330°C (sublimed), (lit.14 mp >315°C). 1H NMR (300 MHz, CDCl3) δ 15.19 (s, 2 H), 8.51 (dd, J = 3.3, 6.0 Hz, 4 H), 7.84 (dd, J = 3.0, 6.0 Hz, 4 H). IR (thin film, CH2Cl2) 3102, 3056, 1624, 1579, 1510, 1464, 1417, 1264, 1045, 862, 725 cm⁻¹.


Crystals for X-ray crystallographic analysis were obtained by slow evaporation of a saturated chloroform solution over about 10 days; diffraction matched the published data.15 6,11-Dihydroxy-5,12-tetracenedione is nearly insoluble in nine common deuterated solvents screened, making 13C NMR data unobtainable.

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