A general approach toward *Janus diones*: synthesis of dicyclopenta[*b,g*]naphthalene-1,3,6,8(2*H*,7*H*)-tetraone

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ABSTRACT

A general approach toward *Janus diones* involving the reaction of pyromellitic or naphthalenetetracarboxylic dianhydrides with ethyl(triphenylphosphoranylidene)acetate and subsequent rearrangement of the products is described. This approach allows avoiding the formation of poorly soluble intermediates, in which purity cannot be effectively controlled. Dicyclopenta[*b,g*]naphthalene-1,3,6,8(2*H*,7*H*)-tetraone **3**, a promising precursor of molecular and polymeric advanced materials is described.

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Recently, we described an efficient synthesis of the elusive *s*-indacene-1,3,5,7(2*H*,6*H*)-tetraone (*Janus dione*) **1**.[1] This compound is a strong electron acceptor and can be used as a precursor for the preparation of reversible multi-stage redox systems, such as dianion **2**[2] and highly efficient two-photon absorbing (TPA) chromophores.[3] Moreover, 1,3-indandiones are employed as precursors

naphthalenetetracarboxylic dianhydride with ethyl acetoacetate in the presence of triethylamine in acetic anhydride yielded a complex mixture of insoluble products. One of the problems was that 2,3,6,7-naphthalenetetracarboxylic dianhydride, as described in,[5] appeared to be not the individual compound. However, using the pure samples of the dianhydride[6] also did not afford acceptable

1　　　**2**　　　**3**
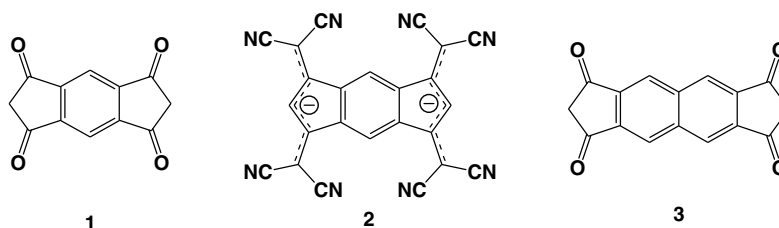
for the preparation of C$_{60}$ and higher fullerenes (see[4] and references cited therein), and using the symmetrical *Janus diones* opens new flexible synthetic routes. From this point of view, hitherto unknown naphthalene-derived analogue (dicyclopenta[*b,g*]naphthalene-1,3,6,8(2*H*,7*H*)-tetraone) **3** presents a special interest as a full fragment of the C$_{60}$ molecule.

Our first attempts to prepare **3** using the same method employed for the synthesis of **1** failed. The condensation of 2,3,6,7-

yields of the desired product. Therefore, we investigated different approaches, in particular, the rearrangement of ylidene derivatives **4a** and **4b**, which are easily available by the Wittig reaction of 2,3,6,7-naphthalenetetracarboxylic dianhydride with ethyl(triphenylphosphoranylidene)acetate[7] (Scheme 1).

Herein, we report on a simple and general approach applicable for the preparation of a variety of 1,3-indandione derivatives, in particular those that are especially prone to self-condensation like *Janus diones* **1** and **3**.

Phthalylideneacetic acid rearranges into unstable 1,3-indandione-2-carboxylic acid in the presence of alcoholates.[8] We found that

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Scheme 1.
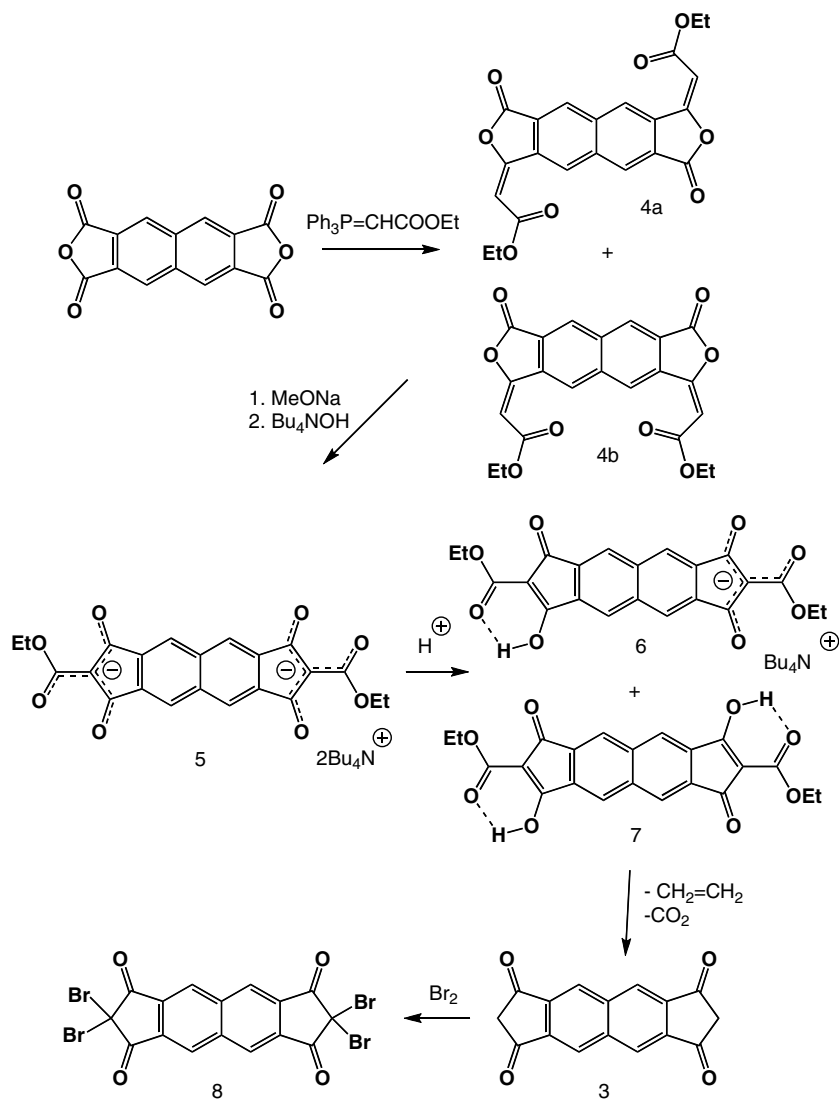
the rearrangement of ester derivatives **4a** and **4b**, both as individual compounds and as a mixture, can also be achieved with sodium methanolate in a high yield. However, the resulting disodium salt is only poorly soluble and its purity cannot be effectively controlled. Therefore, conversion of the disodium salt into the more soluble TBA salt **5** is desirable to prevent the formation, upon acidification, of the mono-anionic salt **6**, which is practically insoluble in water and organic solvents.[9] The rearrangement can also be achieved using TBA hydroxide, however, in this case we observed the formation

of considerable amounts of salt **6**. Neutralization of this salt requires prolonged action of an acid, and thus is accompanied by the formation of **3** and its further immediate polymerization.

Acidification of **5** dissolved in acetonitrile afforded diester **7**. Refluxing **7** in anhydrous acetonitrile led to slow precipitation of **3** as colorless leaflets.[10] This compound is poorly soluble in organic solvents, insoluble in water and, like the most of 2-unsubstituted 1,3-indandione derivatives, easily undergoes self-condensation in the presence of acids and bases. Following the same procedure,
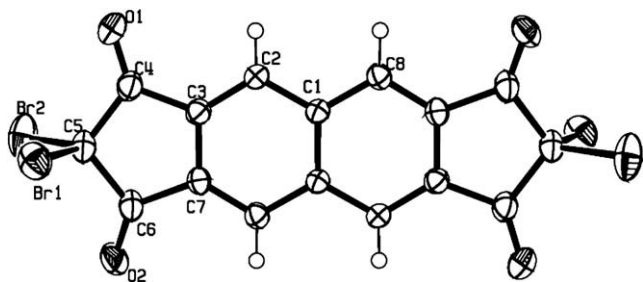

$R_1 = CH_2COOEt$
$R_2 = C_{16}H_{33}$
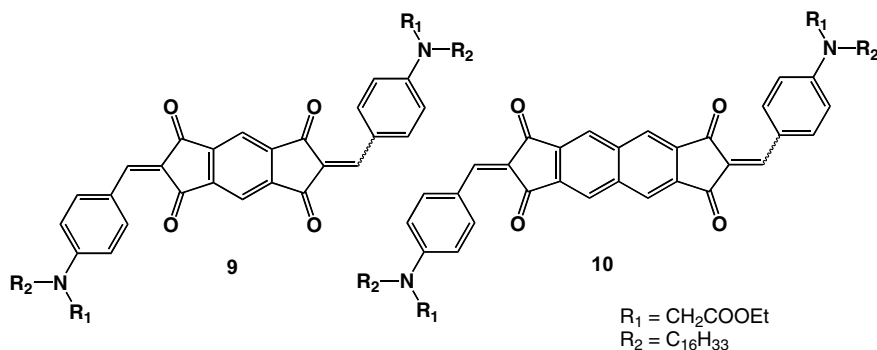
Figure 1. Ortep plot of **8** at 50% probability level. Selected distances in Å: C1–C2 1.414(5); C2–C3 1.371(5); C3–C4 1.474(5); C4–C5 1.539(6); C3–C7 1.411(5); C4–O1 1.200(5); C5–Br1 1.938(4).
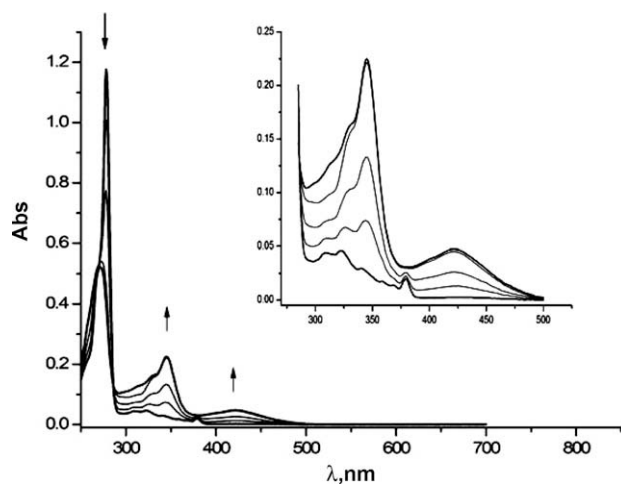

Figure 2. Changes in the absorption spectrum of **3** in methylene chloride upon consecutive addition of DBU (up to 2 equiv). The 300–500 nm range is shown in the inset.

derivative **1** can be prepared from the corresponding ylidene derivatives, which are readily available from pyromellitic anhydride[7], in 75% overall yield.

Bromination of **3** afforded 2,2,7,7-tetrabromodicyclopenta[b,g]naphthalene-1,3,6,8(2H,7H)-tetraone **8**, the structure of which has been confirmed by the X-ray analysis[11] (Fig. 1). This compound is a strong brominating agent: even gentle heating of its acetone solutions leads to the formation of bromoacetone as evidenced by the ^{1}H NMR spectrum.

Derivative **3** in methylene chloride exhibits a number of weak vibronically split bands around 360 nm and a strong sharp absorption band at about 290 nm (Fig. 2).

The dianion of **3** can be generated in solution by addition of 2 equiv of a base. It features a broad band around 430 nm in dichloromethane (Fig. 2), showing thus a considerable blue shift compared to absorption of the dianion of **1** (500 nm).[1]

Similar to compound **1**, derivative **3** easily condenses with *p*-dialkylaminobenzaldehydes in acetic acid upon reflux, affording the corresponding conjugated donor–acceptor–donor derivatives **9** and **10**.[12] Both chromophores exhibit strong charge transfer absorption bands at 535 and 540 nm (in toluene), respectively. An interesting feature of two-photon absorption of **10** is the presence of two equally strong absorption bands at 772 and 974 nm with the cross-section coefficient about 1000 GM. The

detailed account of the TPA properties of derivatives **9** and **10** will be published elsewhere.

In summary, the rearrangement of derivatives **4** in the presence of sodium methanolate and using the soluble TBA salt **5** enable the preparation of both known *Janus dione* **1** and new derivative **3** in high yields. Both compounds are valuable precursors for the synthesis of molecular and polymeric advanced materials.

Acknowledgments

References and notes

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9. Sodium methanolate solution was prepared by dissolving sodium (0.07 g, 3.06 mmol) in dry methanol (3 ml). This solution was rapidly added to a suspension of a mixture of **4a** and **4b**[7] (0.50 g, 1.23 mmol) in methanol (20 ml) at room temperature. After refluxing for 5 h, the reaction mixture was cooled down to room temperature. The yellow precipitate was isolated by filtration, washed with methanol (5 ml), and dried to give the intermediate disodium salt (0.54 g). The disodium salt was suspended in water (40 ml), and a 40% methanol solution of TBA hydroxide (2.38 g, 3.68 mmol) was added. After stirring for 30 min at room temperature, the orange precipitate was filtered, washed with water (10 ml), and dried to give **5** (0.91 g, 83%). This decomposes above 210 °C without melting.
   ^{1}H NMR (DMSO-d_6): δ 7.80 (4H, s), 4.00 (4H, q, ^3J = 7.1 Hz), 3.06–3.22 (16H, m), 1.44–1.64 (16H, m), 1.22–1.36 (16H, m), 1.17 (6H, t, ^3J = 7.1 Hz), 0.91 (24H, t, ^3J = 7.2 Hz).
10. Concentrated hydrochloric acid (0.12 ml of 37% HCl, 1.46 mmol) was added to a solution of **5** (0.50 g, 0.56 mmol) in acetonitrile (30 ml) at room temperature. The yellow precipitate of **7** was filtered, washed with acetonitrile (5 ml), and dried at room temperature (0.22 g, 97%). A suspension of **7** (0.20 g, 0.49 mmol) in anhydrous acetonitrile (50 ml) was heated under reflux until the yellow suspension dissolves (about 30 min). Pure **3** (0.12 g, 92%) crystallized upon cooling as colorless leaflets, which were collected by filtration and dried. Compound **3** sublimes above 290 °C without decomposition. ^{1}H NMR (CDCl$_3$): δ 8.78 (4H, s), 3.46 (4H, s).
11. Bromine (0.47 ml, 9.17 mmol) was added to a suspension of **3** (0.06 g, 0.23 mmol) in DMSO/H$_2$O (1:1.4 ml). The reaction mixture was stirred at room temperature for 2 h. The light orange precipitate was filtered off, washed with water, and dried. The crude **8** (0.12 g, 91%) was crystallized from methylene chloride to afford colorless prisms, which turned brown at 210 °C and melted above 290 °C. ^{1}H NMR (THF-d_8): δ 9.13 (4H, s). ^{1}H NMR (acetone-d_6): δ 9.31 (4H, s). ^{13}C NMR (THF-d_8): δ 187.12 (4 × C), 141.40 (4 × C), 134.62 (4 × C), 130.39 (4 × CH), 53.22 (2 × CBr2).
   Crystallographic data were collected on Bruker-Nonius KappaCCD diffractometer with MoKα radiation, λ = 0.71073 Å, C$_{16}$H$_4$Br$_4$O$_4$. Unit cell parameters: a 13.3498(3); b 12.3157(2); c 10.1692(2), space group *Pbca*. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number CCDC 698427.
12. Compound **9**: a green solid, mp 260 °C (yield 71%). ^{1}H NMR (CDCl$_3$): δ 8.55 (4H, d, ^3J = 9.0 Hz), 8.34–8.40 (2H, m), 7.84 (2H, s), 6.70 (4H, d, ^3J = 9.0 Hz), 4.23 (4H, q, ^3J = 7.1 Hz), 4.16 (4H, s), 3.44–3.56 (4H, m), 1.12–1.42 (62H, m), 0.87 (6H, t, ^3J = 7.1 Hz).
   Compound **10**: a green solid, mp 280 °C (yield 73%). ^{1}H NMR (CDCl$_3$): δ 8.61 (4H, d, ^3J = 8.9 Hz), 8.56–8.58 (4H, m), 7.89 (2H, s), 6.71 (4H, d, ^3J = 8.9 Hz), 4.24 (4H, q, ^3J = 7.1 Hz), 4.16 (4H, s), 3.46–3.56 (4H, m), 1.17–1.34 (62H, m), 0.87 (6H, t, ^3J = 7.1 Hz).