



# The synthesis of lactone-bridged 1,3,5-triphenylbenzene derivatives as pi-expanded coumarin triskelions



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## ABSTRACT

Two triply lactone-bridged 1,3,5-triphenylbenzene derivatives with solubilizing moieties have been synthesized in five and six steps from commercially available starting materials. Compounds containing the 1,3,5-triphenylbenzene core with two atom bridges are relatively unknown. This new class of pi-expanded coumarins contain triskelion architectures and X-ray crystallographic studies of one of the triskelions indicates that the 1,3,5-triphenylbenzene core adopts a near-planar geometry. This is the only known example of a two atom-bridged 1,3,5-triphenylbenzene derivative to adopt a planar structure.

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## Introduction

Large highly conjugated organic molecules with restricted bond rotation have long fascinated chemists because of their unique and attractive optical and electronic properties. It is known that enforcing rigidity and planarity in conjugated pi-systems typically results in more efficient absorption and emission of light<sup>1</sup> as well as improved electronic conductance.<sup>2</sup> Biphenyl is the simplest conjugated system to contain multiple arene units connected by a single bond. However, biphenyl is not a rigid or planar molecule, with solution-phase dihedral angles measured to be between 30 and 40°, depending on the solvent.<sup>3</sup> Our group has been interested in bridging aryl-aryl bonds with lactone units, in the form of new pi-expanded coumarins,<sup>4</sup> to force rigidity and planarity in the aryl-aryl molecular structures.<sup>5</sup> Our previous efforts in this area have been to study the effects of restricting aryl-aryl bond rotation in various biphenyls<sup>5a</sup> and C<sub>2h</sub> symmetric *p*-terphenyl crankshaft-shaped systems<sup>5b</sup> with one and two lactone bridges, respectively, resulting in new pi-expanded coumarin structures. We found that the presence of lactone bridging units greatly enhances both optical absorption and emission relative to their lactone-cleaved analogs.

Branched pi-conjugated small molecules and dendrimers with arene cores have been previously synthesized and studied for pos-

sible application in organic solar cells, field-effect transistors, light-emitting diodes, and non-linear optical devices.<sup>6</sup> Within this class of molecules, many triply-bridged triskelion-shaped C<sub>3h</sub> symmetric compounds containing the 1,3,5-triphenylbenzene core unit have also been synthesized (Fig. 1).<sup>7,8,11</sup> Derivatives of 1,3,5-triphenylbenzene containing one atom bridges, such as truxene and its analogs,<sup>7</sup> have been known for many years and are widely studied. Many derivatives of these structures have also been recently synthesized, many with promising optical and electronic properties.<sup>8,9</sup> Interestingly, despite containing the fluorene moiety (fluorescence quantum yield ( $\Phi_F$ ) = 0.80),<sup>10</sup> truxene itself is only weakly fluorescent ( $\Phi_F$  = 0.07).<sup>8m</sup> However, appending arene units to the basic truxene structure has resulted in highly fluorescent compounds with two-photon absorption properties, non-linear optical properties and potential for application in organic light-emitting diodes (OLEDs).<sup>8g-k,9</sup> Despite its early synthesis, truxenone<sup>7b,7c</sup> and many of its derivatives had been poorly studied because to its poor solubility<sup>8e</sup> due to planarity and aggregation. However it has been incorporated as a starting point for the synthesis of many interesting molecules with potential use as photovoltaic devices, NLO materials, and semiconductors.<sup>8b,8d-f</sup> Trioxatruxene<sup>7d</sup> and its derivatives,<sup>8l</sup> having only been synthesized in very small yields, are currently less well studied. Triazatruxene has been synthesized<sup>7e</sup> and its derivatives studied as the core unit for organic solar cells.<sup>8a</sup> Unlike the numerous single-atom bridged systems described above, synthesis of triskelion shaped 1,3,5-triphenylbenzene compounds with two

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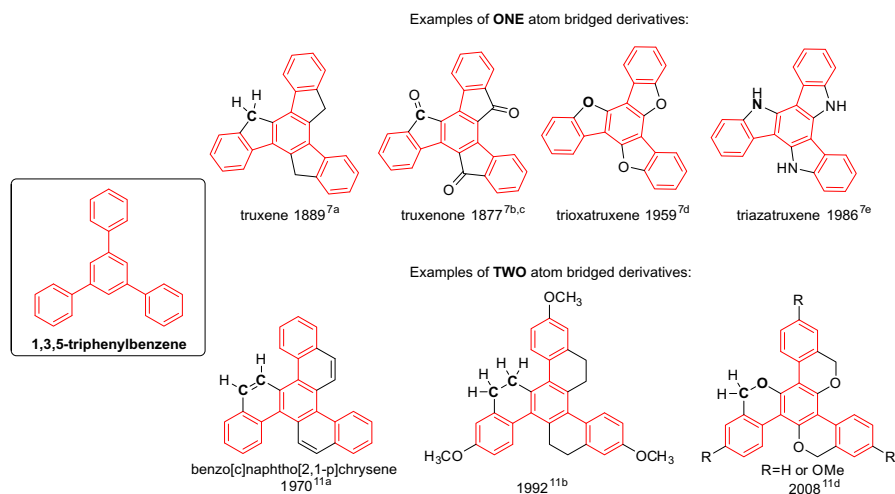


Fig. 1. Examples of known triply-bridged 1,3,5-triphenylbenzene triskelions.

atom bridges (C–O, CH<sub>2</sub>–CH<sub>2</sub>, and CH=CH are known) have been quite rare and some only with limited characterization studies.<sup>11</sup> The large majority of these structures are based on the twisted benzo[c]naphtho[2,1-p]chrysene motif with CH=CH bridges.<sup>11a,11e–i</sup> None are known to be planar compounds.

We were interested in further exploring branched variations of the lactone-bridged oligophenyls previously studied by our group.<sup>5</sup> We desired to expand our knowledge of these unique structures by synthesizing and analyzing two-dimensional triskelion-shaped analogs of the linear lactone-bridged biphenyls and terphenyls (Fig. 2). Given the dearth of 1,3,5-triphenylbenzene derivatives with two atom bridges and complete lack of those with known planar structures, the fundamental knowledge obtained from the synthesis and study of these new compounds is important. Two potential “bridge-flipped” isomeric pi-expanded coumarins containing 1,3,5-triphenylbenzene cores could be envisioned with

C<sub>3h</sub> symmetry, neither known to date. Compound **1** and its derivatives were chosen as the synthetic targets over the more sterically congested “bridge-flipped” isomers in this study due to their predicted planarity relative to the isomeric form and more accessible syntheses. In the “bridge-flipped” isomer of **1** it would be predicted that the carbonyl unit would have unfavorable steric interactions with the adjacent arene C–H, thus affording a twisted structure. In the proposed triskelion **1**, the carbonyl unit is away from the adjacent ring and the oxygen should be small enough to avoid significant steric interactions with the adjacent arene C–H.

## Results and discussion

We initially embarked to synthesize the most basic variation of a triskelion-shaped pi-expanded coumarin: previously unexplored C<sub>3h</sub> symmetric tri-lactone bridged 1,3,5-triphenylbenzene derivative **1** containing no additional substituents (Scheme 1). To synthesize **1**, it was ascertained that benzylic oxidation of known triether **6** should result in **1** in only three steps from commercially available starting materials. Attempts to achieve **6** replicating a known procedure<sup>11d</sup> of triple ether formation from phloroglucinol followed by intramolecular Heck coupling were met with unacceptable yields in our hands. This was optimized by replacing phloroglucinol with triacetoxylbenzene (**4**) to avoid C-alkylation during the triple ether formation.<sup>12</sup> The addition of tricyclohexylphosphine<sup>13</sup> in the subsequent triple Heck coupling to achieve **6** also led to improved yields. Oxidation of **6** with excess PCC<sup>14</sup> afforded a white solid but, to our disappointment, was completely insoluble in all organic solvents, including DMSO, diethyl ether, dichloromethane, chloroform, and toluene. By contrast, the immediate precursor to **1**, previously reported triskelion-shaped triether **6**, had excellent solubility in many organic solvents. The poor solubility of **1**, likely due to the planarity and rigidity of the structure inducing efficient pi-stacking and aggregation, meant that it could not be chromatographically purified or characterized using solution-phase techniques, primarily NMR spectroscopy. Since compounds containing the basic structure of **1** were completely unknown, we set out to produce analogs with more tractable properties.

Given the known utility of *t*-butyl groups for improving solubility of polycyclic aromatic hydrocarbons in our own work<sup>5b</sup> and others,<sup>15</sup> triskelion **2** was designated as the next target (Scheme 2). The placement of the *t*-butyl group *meta* to the aryl-aryl bond in **2** was largely due to synthetic convenience: 4-*tert*-butyltoluene is

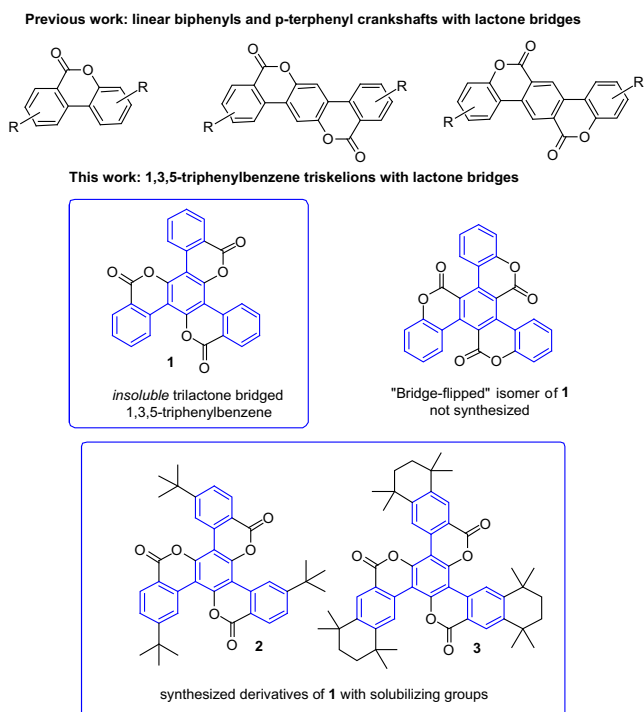


Fig. 2. C<sub>3h</sub> symmetric trilactone bridged 1,3,5-triphenylbenzene triskelions.

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