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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.

Graphical abstract

Keywords

branched molecules; coumarins; extended conjugation; planar geometry; triskelions

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Supplementary Data.

For detailed synthetic procedures for known (4–7, and 10) and new (2, 3, 8, 9, and 11–13) compounds, copies of ¹H and ¹³C NMR spectra for new compounds (2, 3, 8, 9, and 11–13), ¹H NMR spectra of 3 in CD₂Cl₂ and TFA-D, and crystallographic data for 13 and 3 see the supporting information.

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 light¹ as well as improved electronic conductance.² 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 30–40°, depending on the solvent.³ Our group has been interested in bridging aryl-aryl bonds with lactone units, in the form of new pi-expanded coumarins,⁴ to force rigidity and planarity in the aryl-aryl molecular structures.⁵ Our previous efforts in this area have been to study the effects of restricting aryl-aryl bond rotation in various biphenyls^{5a} and C_{2h} symmetric *p*-terphenyl crankshaft-shaped systems^{5b} 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 possible application in organic solar cells, field-effect transistors, light-emitting diodes, and non-linear optical devices.⁶ Within this class of molecules, many triply-bridged triskelion-shaped C_{3h} symmetric compounds containing the 1,3,5-triphenylbenzene core unit have also been synthesized (Figure 1).^{7,8,11} Derivatives of 1,3,5-triphenylbenzene containing one atom bridges, such as truxene and its analogs,⁷ 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.^{8,9} Interestingly, despite containing the fluorene moiety (fluorescence quantum yield (Φ_F) = 0.80),¹⁰ truxene itself is only weakly fluorescent (Φ_F = 0.07).^{8m} 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).^{8g-k,9} Despite its early synthesis, truxenone^{7b,c} and many of its derivatives had been poorly studied because to its poor solubility^{8e} 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.^{8b,d-f} Trioxatruxene^{7d} and its derivatives,^{8l} having only been synthesized in very small yields, are currently less well studied. Triazatruxene has been synthesized^{7e} and its derivatives studied as the core unit for organic solar cells.^{8a} Unlike the numerous single-atom bridged systems described above, synthesis of triskelion shaped 1,3,5-triphenylbenzene compounds with two atom bridges (C-O, CH₂-CH₂, and CH=CH are known) have been quite rare and some only with limited characterization studies.¹¹ The large majority of these structures are based on the twisted benzo[c]naphtho[2,1-p]chrysene motif with CH=CH bridges.^{11a,e-i} 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.⁵ 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 (Figure 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_{3h} 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_{3h} 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^{11d} 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 triacetoxybenzene (**4**) to avoid C-alkylation during the triple ether formation.¹² The addition of tricyclohexylphosphine¹³ in the subsequent triple Heck coupling to achieve **6** also led to improved yields. Oxidation of **6** with excess PCC¹⁴ 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^{5b} and others,¹⁵ 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 inexpensive and widely available commercially whereas 3-*tert*-butyltoluene is not. Following known protocols¹⁶ 4-*tert*-butyltoluene was brominated sequentially on both the aromatic ring and the benzyl carbon with sodium bromate and sodium bisulfite though a simple change in solvent, resulting in **7**. Triple-ether formation of **7** with phloroglucinol gave **8** in reasonable yields, albeit requiring a 48 h reaction time. Triple Heck coupling and subsequent benzylic oxidation with excess PCC and celite resulted in triskelion pi-expanded coumarin **2** in five total synthetic steps.

Triskelion **2** had only slightly improved solubility compared with **1** but, fortunately, it could be adequately characterized using solution phase techniques. However, after testing numerous solvents it was found that **2** was only very slightly soluble in dichloromethane and chloroform, and was effectively insoluble in all other solvents thus making it only a minor improvement compared to **1**. Other attempts by our group to synthesize analogous triskelion-shaped compounds containing other commonly used solubilizing groups, triisopropylsilylacetylene or oligoethylene glycol, were unfortunately fruitless. We discovered that both of these groups were incompatible with the harsh PCC oxidation step, resulting in decomposition. This prompted a synthesis of triskelion **3** which was anticipated to be more robust to reaction conditions, retain the same structural rigidity in its 1,3,5-triphenylbenzene core, and more amenable to characterization and further studies.

Although less common than *t*-butyl groups, 1,1,4,4-tetramethylbutylene fused-ring based moieties are also known¹⁷ to greatly help solubilize polycyclic aromatic hydrocarbons, and should also be inert to the strongly oxidizing conditions used in the synthesis of **2**. To our excitement, triskelion pi-expanded coumarin **3** was readily synthesized in six steps from commonly available starting materials (Scheme 2). Arene **10** was prepared in two steps starting from 2,5-dimethyl-2,5-hexanediol following a literature protocol.¹⁸ Benzylic bromination from NaBrO₃/NaHSO₃ then resulted in **11**. Triskelion **3** was then afforded as previously described for **1** via a triple ether formation and triple Heck coupling in six total synthetic steps. The addition of 1,1,4,4-tetramethylbutylene solubilizing groups improved solubility with **3** being more soluble in dichloromethane, chloroform, and toluene.

Unlike **1** and **2**, Triskelion **3** was easily characterized by ¹H NMR spectroscopy. Comparison of the chemical shifts of the aromatic H signals of **3** and its immediate precursor **13** clearly shows the increased rigidity that the newly added carbonyl groups impart. The aromatic H signals are significantly downfield in **3** (9.54 ppm and 8.45 ppm) compared to **13** (8.26 ppm and 7.18 ppm) due to steric compression induced by planarization of the ring-system. Less soluble triskelion **2** (9.57, 8.31, and 7.79 ppm) also displays a similar downfield shift in aromatic H signals relative to precursor **9** (8.41, 7.38, and 7.23 ppm). Similar steric compression effects have been observed in our previous studies on crankshaft terphenyl dilactones^{5b} and other congested highly-conjugated arene systems.¹⁹

To obtain more direct evidence of the planarity-inducing effects of the carbonyl group on these systems, X-ray crystal studies were desirable. After numerous attempts, **2** could not be sufficiently crystallized in our hands due to poor solubility. However, the improved solubility of **3** allowed for preparation of X-ray quality crystals, grown successfully though very slow evaporation in dichloromethane. To compare the effect of ether and lactone bridges on the structures of triskelion shaped 1,3,5-triphenylbenzene, single-crystal X-ray diffraction was performed on both ether-bridged precursor **13** and lactone-bridged triskelion **3** (see supplementary data). The effect of the lactone bridging unit on flattening the structure of 1,3,5-triphenylbenzene is dramatic. The average aryl-aryl dihedral angle between each peripheral arene ring and the central benzene core found in the X-ray structure of **3** is 5.9°. Precursor **13** is considerably less planar with average aryl-aryl dihedral angles of 24.7°, resulting in a significant twist. The sp² hybridized carbonyl in the bridges of **3** flattens the

aryl-aryl units much more effectively than the sp^3 hybridized methylene in the bridges of **13**. Additionally, triskelion **3** also has the opportunity to become planar relative to the known two-atom bridged (CH=CH) compound benzo[c]naphtho[2,1-p]chrysene (Figure 1), because the oxygen in the bridge of **3** is much smaller than the arene CH unit in the latter. In benzo[c]naphtho[2,1-p]chrysene, the arene CH has a significant steric interaction with the adjacent ring, forcing it to twist, whereas the O on **3** is much smaller and allows the adjacent ring to lay flat. Comparing **3** to the known crystal structure of unbridged 1,3,5-triphenylbenzene²⁰ is also significantly twisted with average aryl-aryl dihedral angles of 28.3° . While the ether bridges in **13** will undoubtedly restrict aryl-aryl rotation relative to no bridge at all, they have little effect on the overall geometry of the 1,3,5-triphenylbenzene core. The lactone bridges in **3** also restrict aryl-aryl rotation but, by contrast, are much more effective at flattening the structure of 1,3,5-triphenylbenzene. Triskelion **3** has a very unique structure in that it is the only two atom-bridged 1,3,5-triphenylbenzene derivative shown to have a near-planar core synthesized to date.

To determine how the introduction of the carbonyl group affects the optical properties of triskelions **2** and **3**, UV-vis and fluorescence spectroscopy studies were done. Comparing the UV absorption spectra of the compounds in this study (Figure 3a and Table 1), it is seen that introducing lactone units (**2** and **3**) results in a significant bathochromic shift (roughly 30 nm in both cases) relative to the compounds containing only ether bridging units (**9** and **13**). This is the result of the presence of the more electron withdrawing carbonyl unit and also **2** and **3** being more planar than **9** and **13**, leading to more efficient conjugation between the outer arenes and central arene core. Both bridging units result in a bathochromic shift relative to unbridged 1,3,5-triphenylbenzene with a known absorption $\lambda_{\text{max}} = 250$ nm in cyclohexane.²¹

Diminished fluorescence quantum yields of *meta*-branched oligophenylenes compared to linear *para*-oligophenylenes is known.¹⁰ This is due to the cross conjugated meta orientation of the phenyl groups in the branched systems leading to attenuated total conjugation across the entire system, thus making the branched systems behave more like biphenyls, rather than terphenyls. Thus, the addition of two or three phenyl rings in meta positions on a central arene (*i.e.* *m*-terphenyl and 1,3,5-triphenylbenzene) has more of an inductive effect on the electronics of the entire system rather than a conjugative effect. For the branched oligophenylene systems containing 1,3,5-triphenylbenzene cores in this study, a similar effect was observed (Figure 3b and Table 1).

Unsubstituted 1,3,5-triphenylbenzene has a known literature emission $\lambda_{\text{max}} = 354$ nm ($\Phi_F = 0.10$) in cyclohexane.²¹ The effect of bridging the aryl-aryl bonds with ether units (**9** and **13**) increases the emission λ_{max} (Table 1). An increase in Φ_F for **13** is also observed but no increase is observed for **9**. The addition of lactone bridges (**2** and **3**) results in a further bathochromic shift of the emission λ_{max} and also the absorption λ_{max} . However, the lactone bridges have a dramatic effect on the fluorescence quantum yields as the Φ_F of both **2** and **3** plummets to near zero, despite the lactone bridge enforcing planarity in the structure. The attenuation in Φ_F could be a result of the known carbonyl-induced fluorescence quenching¹⁰ or the ability of the near-planar lactone systems efficiently pi-stacking, resulting in aggregation induced quenching.²²

Remarkably, upon addition of a small amount of trifluoroacetic acid (TFA) to samples of **2** and **3** in dichloromethane, the Φ_F increases approximately 10-fold and a further small bathochromic shift in emission λ_{max} occurs (Figure 3b and Table 1). The small bathochromic shift is likely due to partial protonation of the carbonyl units. The enhancement in fluorescence was even more pronounced in toluene as the addition of TFA to dilute samples of **3** in toluene led to visible fluorescence under UV irradiation (Figure 4). This result also points to solubility and aggregation caused self-quenching likely playing a role in attenuation of fluorescence of **2** and **3**, since **9** and **13** are both much more soluble than **2** and **3**. It was also observed that solubility of **2** and **3** increases appreciably upon addition of TFA, again, potentially due to decreased aggregation. Partial protonation of the lactone carbonyls by the added TFA could promote the halochromic characteristics of **2** and **3**. Both **9** and **13** were found to decompose in the presence of added TFA, rapidly affording bright red solutions, likely due to the facile formation of benzylic carbocations under the acidic conditions. The addition of TFA also results in a small bathochromic shift in the UV-absorption spectra of **2** and **3** (Figure 3a and Table 1).

To further analyze the effect on TFA on the electronics of **2** and **3**, ^1H and ^{13}C NMR spectra were taken in CD_2Cl_2 with added TFA-D (see supplementary data). No decomposition was noted in the NMR spectra of **2** and **3** in the presence of TFA-D. However, a small downfield chemical shift was observed for the aryl H signal nearest to the carbonyl in the ^1H NMR spectrum for the sample in CD_2Cl_2 (8.45 ppm) compared with CD_2Cl_2 + TFA-D (8.53 ppm). A similar small downfield shift was observed for the carbonyl C signal in the ^{13}C spectrum in CD_2Cl_2 (160.15 ppm) and with added TFA-D (163.33 ppm). This general downfield shift of signals from atoms near the carbonyl upon addition of TFA-D is consistent with partial deuteration of the carbonyl units. Thus the partial protonation likely alters the electronic characteristic of **2** and **3** and could also reduce aggregation due to the protonated forms of **2** and **3** repelling each other, leading to improved emission of light.

In summary, two new pi-expanded coumarins (**2** and **3**) have been synthesized in five and six steps. These unique molecules are the first planar triskelion-shaped 1,3,5-triphenylbenzene derivatives containing lactone bridging units and their structures confirmed by X-ray crystallography. The addition of the carbonyl moiety into the structure of these systems has a dramatic effect on their geometries and optical properties, when comparing triskelions **2** and **3** with **9** and **13**. This new class of pi-expanded coumarins are the first examples of planar two-atom bridged compounds containing the 1,3,5-triphenylbenzene core. Despite the addition of solubilizing groups, both triskelion-shaped compounds were found to have relatively poor solubility in most solvents likely due to pi-pi stacking and aggregation. Future studies will be performed to enhance the solubility and optical properties of these promising systems and to explore their ability to act as molecular geometry switches.

Supplementary Material

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Acknowledgments

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Highlights

- The first synthesis of a trilactone-bridged 1,3,5-triphenylbenzene.
- The compound adopts a triskelion shape and has a near planar configuration.
- This is the first example of any 1,3,5-triphenylbenzene derivative with 2-atom bridges that adopts a near-planar configuration.

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

Previous work: linear biphenyls and p-terphenyl crankshafts with lactone bridges

This work: 1,3,5-triphenylbenzene triskelions with lactone bridges

Figure 2.
 C_{3h} symmetric trilactone bridged 1,3,5-triphenylbenzene triskelions

Figure 3.

(a) UV-vis spectra for compounds dissolved in CH_2Cl_2 or CH_2Cl_2 with added TFA. (b) Fluorescence emission spectra for compounds dissolved in CH_2Cl_2 or CH_2Cl_2 with added TFA and excited at 325 nm.

Figure 4. Photographs of samples under irradiation with a UV lamp: (a) 10 mg of triskelion **3** in toluene. (b) 10 mg of triskelion **3** in 5% TFA in toluene. (c) 5% TFA in toluene with no other solute.

Scheme 1.
Attempted Synthesis of Unsubstituted Triskelion **1**.

Scheme 2.
Synthesis of triskelions **2** and **3**.

Table 1

Electronic absorption and emission data for bridged 1,3,5-triphenylbenzene systems.

compd	lowest E abs λ_{max} [nm] (e [M ⁻¹ cm ⁻¹])	em λ_{max} [nm]	Φ_{F}^c
2^a	320 (28554)	393	0.01
2^b	323 (34638)	403	0.08
3^a	327 (27624)	400	0.01
3^b	330 (28507)	410	0.10
9^a	290 (56535)	387	0.10
13^a	293 (59883)	381	0.21

^aUV-vis spectral data from compounds dissolved in CH₂Cl₂; emission spectral data from compounds dissolved in CH₂Cl₂ and excited at 325 nm.^bUV-vis spectral data from compounds dissolved in 5% TFA in CH₂Cl₂; emission spectral data from compounds dissolved in 5% TFA in CH₂Cl₂ and excited at 325 nm.^cCalculated relative to quinine sulfate dissolved in 0.5 M H₂SO₄ and excited at 325 nm.²³