Stable phenylene- and biphenylene-bis(isobenzofuran)s related to diphenylisobenzofuran

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Abstract: A series of phenyl-substituted bis(isobenzofuran)s in which the furan moieties are linked by 1,3-phenylene, 1,4-phenylene, or 4,4′-biphenylene linkers have been prepared in only two steps. They are comparable to diphenylisobenzofuran in their absorption and luminescent properties, their electrochemistry, and their reactivity. Their degree of similarity to diphenylisobenzofuran was found to depend significantly on the nature of the linking group. Diels–Alder reaction of the title compounds and subsequent aromatization gave very rapid access to penta- or hexa-aryl products.

Key words: isobenzofuran, diphenylisobenzofuran, fluorescence, UV spectroscopy, electrochemistry, pentaphenyl, hexaphenyl.

Résumé : On a préparé, par des réactions n’impliquant que deux étapes, une série de bis(isobenzofuranes) substitués par un groupe phényle dans lesquels les portions furanes sont liées par des tronçons 1,3-phénylène, 1,4-phénylène ou 4,4′-biphénylène. Par leurs propriétés d’absorption et de luminescence, d’électrochimie et de réactivité, ces produits se comparent au diphénylisobenzofurane. On a observé que leur degré de similarité avec le diphénylisobenzofurane dépend beaucoup de la nature du groupe qui les relie. La réaction de Diels–Alder des composés mentionnés dans le titre et l’aromatisation subséquente des produits obtenus donne un accès très rapide aux produits penta- ou hexarylés.

Mots-clés : isobenzofurane, diphénylisobenzofurane, fluorescence, spectroscopie UV, électrochimie, pentaphényle, hexaphényle.

[Traduit par la Rédaction]

Commercially available 1,3-diphenylisobenzofuran (**1**, Fig. 1) has found wide application in the identification of reactive olefins, as an analytical tool for measuring the rate of singlet-oxygen generation and is of interest for its fluorescence, electrochemical, chemi-, and electro-luminescent properties.[1,2] Examples have also been used as electron-transport materials.[3] The chemistry of the parent hydrocarbon isobenzofuran (IBF, **2**) and its derivatives continues to be of significant interest and has been reviewed regularly.[1,2,4–8]

In view of the many useful properties of **1**, we now wish to report the efficient synthesis of several compounds (**3a**–**3c**, Fig. 1) closely related to **1** but bearing two isobenzofuran moieties linked via one or two aromatic rings. Subsequent elaboration of these compounds into penta- and hexa-aryls is also described. Most preparations of diarylisobenzofurans are based on the addition of Grignard reagents to anhydrides or phthalides.[1,9] This work extends that of a report describing the preparation of teraryls via adducts of phenylenebis(isobenzofuran)s in which the furan species is generated transiently[10] from hemiaminal precursors.[11]

The title compounds were prepared in only two steps (Scheme 1) using an extension of methodology previously developed.[11] Phenyllithium was added to 2-bromobenzaldehyde, and the resulting addition product was metalated with *n*-BuLi. Addition of the appropriate dicyanoaryl gave, after hydrolysis, hemiaminal **4** as a mixture of diastereomers. The ^{1}H NMR spectrum of **4** contained singlets between 6.2 and 6.5 ppm corresponding to the methine protons on the furan ring of diastereomeric products. The oily hemiaminal product was refluxed with *p*-toluenesulfonic acid (TsOH) to form the stable IBFs (**3**) in approximately 50% yield (based on dinitrile).

A second method could also be used to prepare 4,4′-biphenylenebis(3-phenylisobenzofuran) (**3c**) (Scheme 2). Metalation of 4,4′-dibromobiphenyl and reaction of the dianion with 2 equiv. of bromobenzaldehyde was followed by metalation with *n*-butyllithium. Subsequent reaction with benzonitrile followed by hydrolysis gave hemiaminal **5**, confirmed by the appearance of two peaks at 6.24 ppm and 6.42 ppm in the ^{1}H NMR spectrum as for compound **4**. The hemiaminal and a catalytic amount of TsOH were refluxed in methanol to form the stable IBF (**3c**) in 39% yield (from 4,4′-dibromobiphenyl).

The three title compounds are all highly coloured: **3a** is a beautiful blood red, **3b** is orange, and **3c** is yellow. Solutions

Received 21 October 2008. Accepted 18 March 2009. Published on the NRC Research Press Web site at canjchem.nrc.ca on 1 June 2009.

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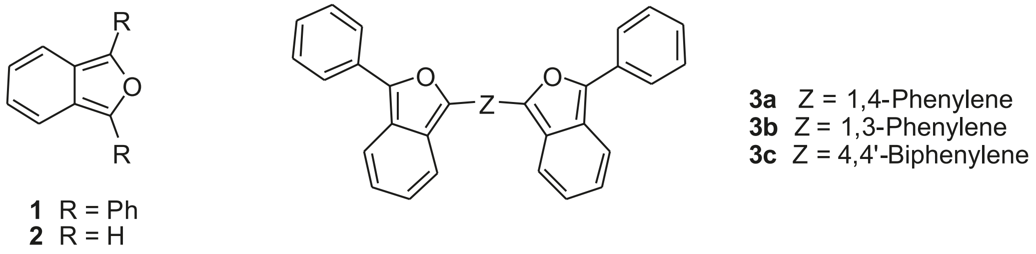
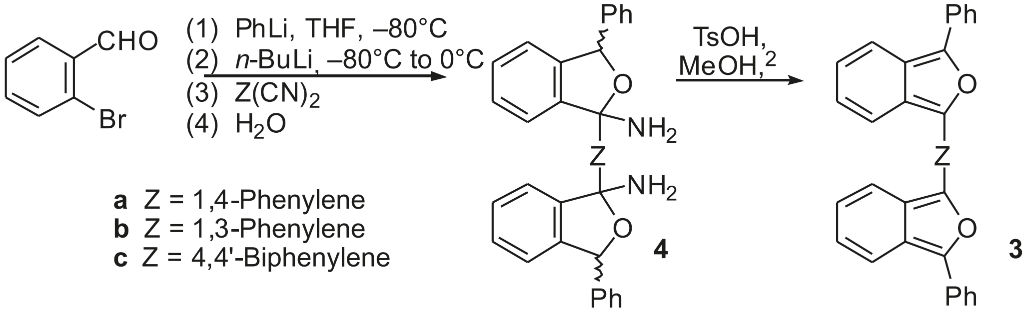
doi:10.1139/V09-063

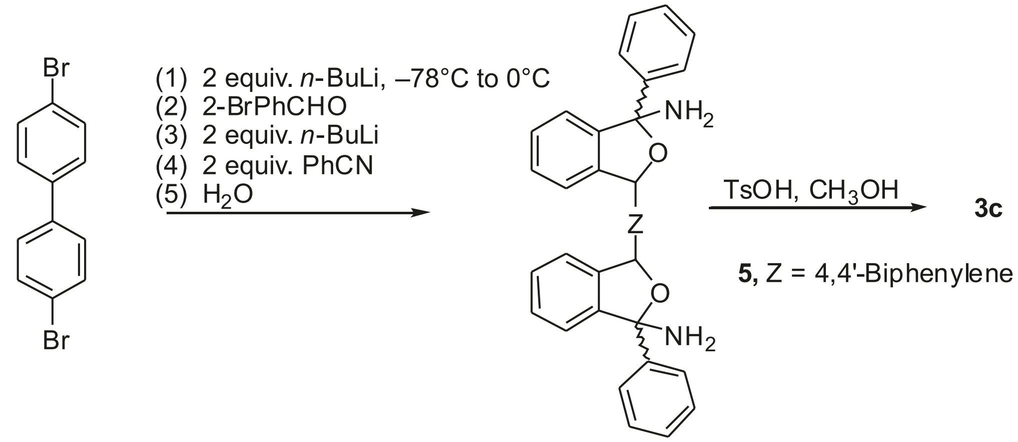
Fig. 1. Stable phenylenebis(isobenzofuran)s.



Scheme 1. Synthesis of **3a**–**3c.**



Scheme 2. Alternative synthesis of **3c**.



of all three compounds are also highly coloured and show the same fluorescent character as **1**, especially when irradiated with long-wavelength UV radiation. Example **3b** resembles **1** most closely in its visible fluorescence in solution.

The NMR spectra of **3** were largely unremarkable. The presence of a ring current in isobenzofurans is well-established, and all of the protons and carbon resonances were found in the aromatic region. In the carbon spectra, the quaternary carbons next to oxygen were found downfield in the 140 ppm region, typical for carbons of this type. In the proton NMR spectra, the typical AA′BB′ patterns of the isobenzofuran rings were obscured by the resonances of the phenyl substituents. Some protons of the central aromatic linker all experience significant downfield shifts: in **3b**, there is a singlet at 8.49 ppm (the proton between the two isobenzofurans); in **3a**, a four-proton singlet appears at 8.10 ppm; in **3c**, the biphenyl protons appear as an AB quartet centered at 7.80 ppm and 8.04 ppm. In **1**, the protons on the phenyl substituents ortho to the isobenzofuran appear at 7.9 ppm. These shifts are likely the result of steric-contact deshielding,[12,13] additive in the downfield signal of **3b**.

The UV absorbances for **1** and **3a**–**3c** are given in Table 1. For **1**, there are two principal bands at 415 and 261 nm. The latter band is common to all of **3a**–**3c** and is likely due to the phenyl substituents. The longer wavelength band of **1**, attributed to a π–π^* transition[1] is matched by one in **3b**, while in **3c** and **3a**, this band is found at progressively longer wavelength. These, and other data, make it clear that of **3a**–**3c**, it is the meta-substituted **3b** that most closely resembles **1**. Its high-wavelength band is found in the same position as **1**, while the other two examples exhibit significant red shifts expected of extended conjugation. Interestingly, of **3a** and **3c**, it is the smaller π-system of **3a** that exhibits the greatest red shift. We attribute this to steric hindrance about the biphenyl linkage that inhibits coplanarity of the π-systems, a structural feature that is absent in **3a**.

Emission data for this series of compounds are presented in Table 2. The luminescence properties of diarylisobenzo-

Table 1. UV–vis spectral data (λ_{max}, nm, $c = 10^{-5}$mol/L).

1 (Ether)[1]	**3a** (MeOH)	**3b** (Dioxane)	**3c** (Dioxane)
275 (4.5)	261 (4.7)	256 (4.6)	270 (4.3)
310 (3.95)	313 (4.3)	321 (3.8)	—
415 (4.45)	473 (4.4)	413 (4.1)	447 (3.9)

Table 2. Emission data for **1** and **3a**–**3c** (λ_{max}, nm, $c = 10^{-5}$ mol/L).

	1 (Hexane)[14]	**3a** (MeOH)	**3b** (MeOH)	**3c** (MeOH)
Excit. wavelength	—	476	416	270
	—	—	—	333
	458	566	461	507
	480	—	480	540
Stokes shift	43	93	48	60

Table 3. Electrochemical data for **1** and **3**.

	0/+ (V)	0/– (V)	–/2– (V)	2–/3– (V)	3–/4– (V)
1	0.75	–1.98	–2.52	—	—
3a	0.81	–1.69	–1.85	–2.43	–2.73
3b	—[a]	–2.06	–2.24	–2.68	–2.87[b]
3c	—[a]	–2.33	–2.73	–3.01	—

Note: Data were collected in THF solution containing 2 mmol/L NBu_4PF_6, referenced to internal ferrocene, and corrected to the SCE scale.

[a] Not observed (outside of solvent range).

[b] Observed only at –30 °C.

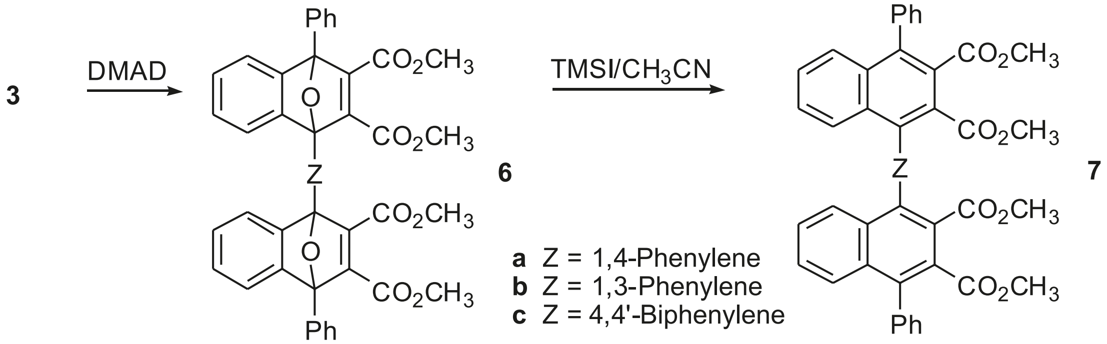
furans have been summarized.[1] The emission spectrum of **3b** is almost identical to that observed for **1**, exhibiting two bands at equal intensity at 461 and 480 nm. The trends for this series of compounds observed in the UV spectra are repeated here. Example **3a** has its fluorescence band shifted to higher wavelength to the greatest extent and appears as a single broad band. Compound **3c** is intermediate between the other two in terms of the position of its principal bands. Its spectrum differs in that it has an additional band at 333 nm (a band corresponding to the fluorescence band of biphenyl) and a shoulder at 470 nm.

The electrochemistry of **1** has been investigated, and we compared its behavior with **3a**–**3c** (Table 3). Compound **3a** shows four reduction processes and one oxidation process. Compounds **3b** and **3c** show four and three reductions, respectively, while **1** has two reductions and one oxidation. The data indicate **3a** is more easily reduced than **1**, but **3b** and **3c** are more difficult to reduce. The mechanism of reduction of **3a** and **3b** can be speculated by comparison with **1**. It can be estimated that the difference between the first reduction potential and the second reduction potential of **1** is in general the potential required to form a doubly reduced IBF dianion from the anion radical. For **1**, the second reduction requires an additional 0.54 V from the anion radical. The difference in potential for $[\mathbf{3a}]^{0/-}$ and $[\mathbf{3a}]^{-/2-}$ is 0.16 V, which is less than that required to form a doubly reduced IBF. This suggests that each IBF in **3a** has been reduced once. The next reduction requires an additional 0.58 V, which corresponds to the potential required to form a doubly reduced IBF. The magnitude of the potential of $[\mathbf{3a}]^{3-/4-}$ is comparable to the second reduction for **1**. A similar comparison can be made for **3b**. The data obtained for **3c** are not consistent with that of the other examples but may be compromised due to poor solubility in THF. The anions produced, excluding the anion formed from the last reduction, are stable under the conditions of the electrochemical experiment and may or may not be stable outside the conditions of the experiment.

The physical appearance, UV–visible spectra, and electrochemical data all show that it is meta-substituted **3b** that most closely resembles **1**. The other examples indicate that the through-conjugated connecting rings offer a better electronic interaction between the IBF moieties. This is seen in the shift of the 415 nm UV band of **1** to lower wavelengths in **3a** and **3c**. It is also consistent with the relative ease of reduction of **3a** in comparison to **3b**. We are interested in preparing polymeric versions of these molecules with alternating phenylene or biphenylene and isobenzofuran rings. These examples suggest that if one desires a polymeric form of **1**, then meta-phenylene linkages will serve to electronically insulate the IBF rings such that they retain the character of **1**. If it is desirable to tune the electronic properties of the IBF rings conjugatively, then through-conjugative linkages will work best.

Not surprisingly, **3a**–**3c** react in a fashion identical to **1**. When refluxed with an excess of dimethyl acetylene dicarboxylate (DMAD), Diels–Alder adducts **6** (Scheme 3) were isolated in yields of 67% to 75%, as mixtures of diastereomers. The presence of a mixture was clear in the case of **4c** where there were many methyl peaks evident in the proton NMR. In the case of **3a** and **3c**, the spectra showed only the number of peaks expected of a single diastereomer.

Scheme 3. Diels–Alder reactions.



There is no reason to expect any diastereoselectivity in this reaction, however, so we conclude that the diastereomers formed in this reaction have identical NMR spectra. The adducts were deoxygenated by treatment with trimethylsilyl iodide[15,16] to form polyaryls **7**. This represents a very efficient synthesis of such molecules in only four steps from commercially available materials.

We did not anticipate, nor did we observe, any difference in reactivity between **3a**–**3c** and their DMAD monoadducts. Significant rate differences in fused difuran systems have been observed.[17] Reaction of **3a** with 1 equiv. of DMAD gave a mixture of monoadduct, bisadduct, and starting material. The presence of the monoadduct during reaction could be observed visually during the Diels–Alder reactions by the presence of the characteristic yellow-green colour of the diphenylisobenzofuran chromophore.

In summary, we have prepared and characterized a series of novel bis(isobenzofuran)s with properties similar to 1,3-diphenylisobenzofuran. The syntheses are efficient and should be easily generalized to other substituted examples. Reaction with DMAD and subsequent aromatization gives rapid access to penta- or hexa-aryl systems.

We have begun to explore the possibilities of preparing polymeric versions of **3** as well as preparing Diels–Alder polymers by reaction of **3** with quinone, DMAD and bis(maleimide) dienophiles. Furan/maleimide polymers have been reported to be self-mending.[18] Other examples of monomers based on diarylisobenzofurans have been reported.[19,20]

Experimental section

Cyclic voltammetric (CV) studies (scan rates N = 20–5000 mV/s) were made with a PAR 173 potentiostat, 175 Universal Programmer and recorded on a Houston Graphics 2000 XY plotter. Electrochemical experiments were performed on a platinum three-electrode system with the platinum working electrode either a 0.5 mm Pt wire or a 0.5 mm diameter Pt micro-tip. A positive feedback circuitry was employed to minimize iR drop losses. The vacuum-tight all glass electrochemical cell has been described in detail elsewhere.[21] The cell was charged with the supporting electrolyte NBu_4PF_6 with solvent THF. Compounds under investigation and ferrocene acting as an internal reference compound were added to the cell using break-seal techniques. Ferrocene was sublimed prior to use.

NMR spectra were recorded on a Bruker AC250 MHz spectrometer unless otherwise indicated. Melting points were performed in open capillaries and are uncorrected. Mass spectra were obtained from the Mass Spectroscopy Lab at the University of Alberta or the Centre for Molecular Architecture, Central Queensland University. Combustion analyses were performed by MHW Labs in Phoenix, Arizona.

1,4-Phenylenebis(1,3-dihydro-3-phenyl-1-isobenzofuranamine), 4a

In 300 mL of dry THF was dissolved 2-bromobenzaldehyde (3.5 g, 19 mmol), purged with N_2, and cooled to –80 °C. Phenyllithium (11 mL of a 1.8 mol/L solution in cyclohexane/ether, 20 mmol) was added by syringe. After 10 min, the reaction was warmed to room temperature. A small aliquot analyzed by proton NMR showed the presence of aldehyde, so an additional 1 mL of phenyllithium was added. After 5 min, the reaction was cooled to –80 °C, and 8.0 mL of 2.5 mol/L *n*-BuLi (in hexanes, 20 mmol) was added. After 15 min, the reaction was warmed to 0 °C, and stirring was continued for 20 min. An aliquot, quenched with water, was analyzed by proton NMR and indicated the loss of bromine. 1,4-Dicyanobenzene (1.09 g, 9.1 mmol) was added to the solution in a single portion, and the solution went dark. The reaction was allowed to warm to room temperature and stirred for 10 h. Water (300 mL) was added, and the reaction mixture was then extracted with diethyl ether (250 mL). The organic phase was separated and dried over $MgSO_4$. After filtration, the solvent was removed under reduced pressure and the residue recrystallized in methanol to give 2.0 g **4a** (63%) as a mixture of diastereomers: mp 90 °C (dec.). ^{1}H NMR (250 MHz, $CDCl_3$) δ: 2.50 (s, 4H, exchanges with D_2O), 6.14 and 6.33 (s, 2H), 6.91–7.51 (m, 18H), 7.72 (s, 4H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 82.9, 83.6, 98.59, 98.62, 98.71, 98.77, 122.28, 122.32, 122.37, 123.08, 123.12, 123.15, 123.3, 125.45, 125.6, 126.3, 126.4, 126.5, 127.2, 128.1, 128.25, 128.31, 128.37, 128.57, 128.64, 128.7, 140.7, 141.1, 141.75, 141.84, 141.86, 143.3, 143.9, 144.11, 144.17, 144.20. IR (KBr): 3391 and 3320, 1264, 1032, 1015, 953, 743 cm^{-1}. MS (EI) *m*/*e*: 478 (4), 462 (100), 295 (23), 231 (23), 165 (22), 154 (39), 85 (51), 83 (78). Analysis calcd. for $C_{34}H_{28}N_2O_2$: C, 82.23; H, 5.68; N, 5.64. Found: C, 82.00; H, 5.40; N, 5.66.

1,4-Phenylenebis(3-phenyl-1-isobenzofuran), 3a

To 120 mL of methanol were added 315 mg (0.64 mmol) of bishemiaminal (**4a**). The solution was brought to reflux, and a total of 240 mg (1.26 mmol) TsOH was added over 5 h. After a further two hours at reflux, the solution was cooled and filtered of a bright red solid. Recrystallization from $CHCl_3/CH_3OH$ gave 222 mg of **3a** (76%). Use of crude hemiaminal **4a** gave a 63% yield from 1,4-dicyanobenzene: mp 216–218 °C. ^1H NMR (250 MHz, CD_2Cl_2) δ: 7.06–7.14 (m, 4H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 4H), 7.88–8.03 (m, 8H), 8.10 (s, 4H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 120.3, 122.4, 122.5, 124.9, 125.0 125.29, 125.35, 127.0, 129.0, 129.7, 131.6, 143.6, 144.0. IR (KBr): 1618, 1493, 829, 760, 683, 657 cm^{-1}. UV–vis ($c = 1.0 \times 10^{-5}$, MeOH) ν_{max}: 261 (4.7), 313 (4.3), 473 (4.4) nm. MS (EI) *m*/*e*: 463 ($M^+ + 1$, 36), 462 (M^+, 100), 385 (2), 231 (20), 209 (51), 165 (6), 105 (10), 77 (11). Analysis calcd. for $C_{34}H_{22}O_2$: C, 88.29; H, 4.79. Found: C, 88.16; H, 4.96.

1,3-Phenylenebis(3-phenyl-1-isobenzofuran), 3b

A solution of 150 mL of dry THF and 1.943 g of 2-bromobenzaldehyde (10.50 mmol) was purged with N_2 and cooled to –80 °C with stirring. After 11.2 mL (15.75 mmol) of 1.4 mol/L Ph-Li was added via syringe, the mixture was warmed to 0 °C and allowed to react for 40 min. At –75 °C, 4.4 mL of *n*-butyllithium was added, and after 15 min, the reaction was warmed to 0 °C and allowed to react for 1 h. 1,3-Dicyanobenzene (0.6727 g, 5.25 mmol) was dissolved in dry THF and added very slowly by syringe, and the mixture was warmed to room temperature, reacting for 16 h. After treatment with H_2O, the mixture was extracted three times with ether, separating and collecting the organic phase. The ether was dried over $MgSO_4$, and then removed by vacuum to leave a brown oil. The oil was dissolved in methanol with TsOH (an equivalent amount) and brought to reflux for 4 h. The orange solid that precipitated out of the reaction mixture was recrystallized in methanol/acetone. The mother liquor was washed with 10% NaOH and extracted three times with chloroform. The organic phase was collected, and the solvent was dried over $MgSO_4$ and removed by vacuum leaving a brown oil. The oil was dissolved in acetone/methanol to give crystalline product **3b** (50%): mp 179–182 °C. ^1H NMR (250 MHz, $CDCl_3$) δ: 7.03–7.12 (m, 4H), 7.26–7.35 (m, 2H), 7.48–7.62 (m, 5H), 7.84–8.00 (m, 10H), 8.49 (s, 1H). ^{13}C NMR (250 MHz, $CDCl_3$) δ: 120.0, 120.7, 120.9, 122.2, 122.4, 123.1, 124.8, 125.2, 125.1, 127.0, 129.0, 129.4, 131.6, 132.2, 143.4, 144.0. IR (Nujol): 652.07, 676.35, 732.9, 763.81, 775.46, 1207.81, 1498.57, 1593.2 cm^{-1}. UV–vis ($c = 1.0 \times 10^{-5}$, dioxane) ν_{max}: 256 (4.6), 321 (3.8), 413 (4.1) nm. MS (EI) *m*/*e*: 462 (M^+, 100), 446 (**3c**), 385 (5), 357 (2), 326 (2), 269 (2), 231 (2). Analysis calcd. for $C_{34}H_{22}O_2$: C, 88.29; H, 4.79. Found: C, 88.10; H, 5.00.

4,4′-Biphenylbis(3-phenyl-1-isobenzofuran), 3c from 4,4′-dibromobiphenyl

In a two-necked round-bottom flask, equipped with a stir bar and stoppers, a mixture of 4,4′-dibromobiphenyl (0.50 g, 1.60 mmol) and dry THF was purged with N_2 and cooled to –80 °C. After *n*-butyllithium (2.5 mol/L, 1.41 mL, 3.53 mmol) was added via syringe, the mixture was warmed to 0 °C and allowed to react for 40 min. At –75 °C, 2-bromobenzaldehyde (0.35 mL, 3.2 mmol) was added dropwise. The mixture was warmed to 0 °C, then to room temperature, and stirred for 16 h. After *n*-butyllithium (2.5 mol/L, 1.4 mL, 3.5 mmol) was added at –75 °C, the mixture was warmed to 0 °C and allowed to react for 40 min. At 0 °C, 0.36 mL (3.53 mmol) of benzonitrile was added. The mixture was warmed to room temperature and allowed to react for 1.5 h leaving a bright red-orange, fluorescent solution. The reaction was quenched with H_2O (120 mL) and extracted three times with ether. The organic phases were collected, dried over $MgSO_4$, and removed under vacuum to leave an orange oil. The yellow oil was dissolved in methanol, with a catalytic amount of PPTS and was brought to reflux with stirring. After 16 h, the reaction showed no change, and TsOH monohydrate was added and the mixture immediately turned from pale green to orange with solid precipitating out of solution. Recrystallization from DMF gave **3c** (39%): mp 296 °C (darkens, dec.). ^1H NMR (250 MHz, CD_2Cl_2) δ: 7.00–7.04 (m, 4H), 7.26 (t, *J* = 7 Hz, 2H), 7.45 (t, *J* = 7 Hz, 4H), 7.77–8.04 (m, 16H). IR (KBr): 657.8, 692.5, 742.6, 761.9, 821.7, 1491.1, 1595.2, 1676.2 cm^{-1}. UV–vis ($c = 9.5 \times 10^{-6}$, dioxane) ν_{max}: 270 (4.3), 447 (3.9) nm. MS (EI) *m*/*e*: 538 (M^+, 100), 346 (35), 269 (14), 239 (16), 209 (17), 105 (25), 77 (20), 73 (57). Analysis calcd. for $C_{40}H_{26}O_2$: C, 89.19; H, 4.87. Found: C, 88.92; H, 4.98.

4,4′-Biphenylenebis(3-phenyl-1-isobenzofuran), 3c from 4,4′-dicyanobiphenyl

In 125 mL of dry THF was dissolved 2-bromobenzaldehyde (2.0 g, 10.8 mmol), and the solution cooled to –80 °C under nitrogen. Phenyllithium (6.0 mL of 1.8 mol/L in cyclohexane, 10.8 mmol) was added by syringe and the mixture warmed to 0 °C for 10 min. *n*-Butyllithium (4.7 mL of 2.5 mol/L in hexanes, 11.8 mmol) was then added. After 10 min, 0.99 g of 4,4′-dicyanobiphenyl was added as a solid in one portion. The solution was allowed to warm to room temperature overnight. Water (100 mL) and diethyl ether (150 mL) were added. The ether phase was separated, dried over anhydrous $MgSO_4$, filtered, and the solvent removed under reduced pressure. The resulting yellow oil (**4c**) had ^1H NMR (250 MHz, $CDCl_3$) δ: 2.4 (br s, 4H), s (5.88, 6.23, and 6.38 in a 1:2.4:1.3 ratio, total 2H), 7.0–7.9 m (26 H). It was not characterized further but was treated with TsOH to form **3c** as described in the preceding paragraph.

Dimethyl 1,4-phenylenebis(1,4-epoxy-1,4-dihydro-4-phenyl-1-naphthalene-2,3-dicarboxylate), 6a

In a 50 mL RBF were placed 67 mg of **3a**, 15 drops of DMAD, and a stirring bar. Dioxane (30 mL) was added, the flask wrapped in foil, and purged with nitrogen. The mixture was stirred for 10 h at which point it was colourless. The solvent was removed by rotary evaporation and the residue crystallized from $CHCl_3/CH_3OH$ to give 72 mg of adduct **6a** (67%): mp 284–287 °C (dec.). ^1H NMR (250 MHz, $CDCl_3$) δ: 3.68 (s, 6H), 3.69 (s, 6H), 7.15–7.17 (m, 4H), 7.47–7.53 (m, 10H), 7.73–7.76 (m, 4H), 7.85 (s, 4H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 52.6, 93.9, 93.9, 94.4, 122.3, 122.5, 126.26, 126.29, 128.23, 128.39, 128.44, 128.8, 129.4, 133.2, 134.2, 149.08, 149.18, 153.95, 154.06, 164.2. IR (Nujol): 1721, 1314, 1262, 1128, 752 cm^{-1}. MS (EI) *m*/*e* calcd. for $C_{46}H_{34}O_{10}$: 746.21521, found: 746.21162; 746 (M$^+$, 2), 670 (51), 604 3b, 462 (38), 439 (50), 297 (38), 231 (18), 105 (100). Analysis calcd. for $C_{46}H_{34}O_{10}$: C, 73.99; H, 4.59. Found: C, 74.06; H, 4.66.

Dimethyl 1,3-phenylenebis(1,4-epoxy-1,4-dihydro-4-phenyl-1-naphthalene-2,3-dicarboxylate), 6b

In a round-bottom flask, **3c** (0.053 g, 0.115 mmol) and DMAD (0.082 g, 0.573 mmol) were dissolved in toluene. As the mixture was allowed to reflux (with stirring) for 2 h, the solution turned from bright yellow to clear. The solvent was removed by rotary evaporation to leave a pale yellow oil. The oil was crystallized in ethyl acetate / petroleum ether to give a 67% yield of **6b**, a white solid: mp 162–170 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 3.65–3.68 (m, 12H), 7.14–7.18 (m, 4H), 7.44–7.61 (m, 11H), 7.72–7.84 (m, 6H), 8.11 (s, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 52.53, 52.56, 94.05, 94.08, 94.21, 94.24, 122.28, 122.36, 126.3, 127.7, 128.2, 128.8, 129.0, 129.1, 129.3, 133.3, 133.9. IR (KBr pellet): 702.08, 755.37, 793.51, 976.44, 1003.12, 1122.84, 1255.91, 1309.09, 1434.14, 1452.68, 1630.93, 1727.95, 2951.15 cm^{-1}. MS (EI) *m/e* calcd. for $C_{46}H_{34}O_{10}$: 746.2152, found: 746.2173; 746 (M$^+$, 0.3), 604 (27), 463 (14), 462 (38), 439 (41), 269 (18), 111 (12), 105 (100). Analysis calcd. for $C_{46}H_{34}O_{10}$: C, 73.99; H, 4.59. Found: C, 74.16; H, 4.70.

Dimethyl 4,4′-biphenylenebis(1,4-epoxy-1,4-dihydro-4-phenyl-1-naphthalene-2,3-dicarboxylate), 6c

In a round-bottom flask, 47.5 mg (0.088 mmol) of **3c** and 0.108 mL (0.882 mmol) of DMAD were dissolved in toluene. The mixture was allowed to reflux with stirring for 0.5 h as the solution turned from orange to lime green to clear. The solvent was removed, and the resulting yellow oil was dissolved in methanol to crystallize. Adduct **6c**, a white solid was obtained in 75% yield: mp 224–228 °C (melt/dec.). ^{1}H NMR (250 MHz, CDCl3) δ: 3.71 (s, 6H), 3.72 (s, 6H), 7.17–7.20 (m, 4H), 7.47–7.56 (m, 10H), 7.72–7.75 (m, 8H), 7.82–7.85 (m, 4H). ^{13}C NMR (250 MHz, $CDCl_3$) δ: 52.58, 52.62, 94.1, 94.3, 122.43, 122.46, 126.3, 127.6, 128.2, 128.8, 129.3, 132.7, 133.3, 141.5, 149.27, 149.33, 153.6, 154.5, 164.3, 164.4. IR (Nujol): 752.3, 1255.7, 1311.7, 1454.4, 1722.5 cm^{-1}. MS (FAB) *m/e*: 823 (MH$^+$, 0.9), 791 (2.4), 680 (2.1), 538 (2.5), 515 (2.9), 309 (5.1), 155 (39.7), 135 (48.7), 119 (100), 105 (73.1). Analysis calcd. for $C_{52}H_{38}O_{10}$: C, 75.90; H, 4.65. Found: C, 75.89; H, 4.86.

Dimethyl 1,4-phenylenebis(4-phenyl-1-naphthalene-2,3-dicarboxylate), 7a

Adduct **6a** (0.23 g, 0.32 mmol) and NaI (0.29 g, 1.9 mmol) were dissolved in 30 mL of dry acetonitrile. Trimethylsilyl chloride (0.25 mL, 1.9 mmol) was added by syringe and the mixture refluxed for 2 days. An equal volume of water was added and the mixture extracted twice with 50 mL of chloroform. The combined chloroform extracts were washed with 10% $NaHSO_3$ solution and dried over $MgSO_4$. The solvent was removed and the residue columned on 4 inches of silica eluting with chloroform graded to 1% ethyl acetate in chloroform. The fractions containing the product were stripped of solvent, and the product was precipitated by the addition of methanol. Filtration gave 0.17 g of **7a** (78%): ^{1}H NMR (250 MHz, $CDCl_3$) δ: 3.45 (6), 3.58 (6), 7.4–7.8 (m, 22H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 52.5, 53.5, 127.4, 127.7, 128.0, 128.1, 128.3, 129.0, 129.3, 129.97, 130.01, 132.8, 133.0, 137.45, 137.53, 137.7, 138.7, 139.5, 168.8, 168.9. IR (KBr): 1741 and 1726, 1436, 1241, 1221, 1130, 773, 702 cm^{-1}. MS (EI) *m/e* calcd. for $C_{46}H_{34}O_8$: 714.2253, found: 714.2267; 714 (M$^+$, 100), 651 (18), 326 (10), 87 (5).

Dimethyl 1,3-phenylenebis(4-phenyl-1-naphthalene-2,3-dicarboxylate), 7b

Adduct **6b** (0.43 g, 0.58 mmol) and NaI (0.43 g, 2.9 mmol) were dissolved in 50 mL of dry acetonitrile under nitrogen. The solution was cooled to 0 °C and TMSCl (0.37 mL, 2.9 mmol) added by syringe. The solution was then stirred at room temperature for 24 h. Saturated $NaHSO_3$ was added, and the solution was extracted twice with 50 mL portions of chloroform. The organic phase was separated, dried over $MgSO_4$, and stripped of solvent. The residue solidified and was recrystallized from methanol to give, in several crops, a total of 0.32 g (78%): mp 214–215 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 3.52 (3.67 and 3.68, *J* = 3s Hz, 12H), 7.33–7.78 (m, 22H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 52.32, 52.35, 52.5, 52.6, 127.3, 127.5, 127.6, 127.7, 127.8, 127.95, 127.98, 128.90, 128.08, 128.13, 128.18, 128.24, 128.27, 128.33, 128.4, 128.8, 129.01, 129.07, 129.21, 129.5, 129.98, 130.13, 130.2, 130.3, 131.7, 132.2, 132.89, 132.95, 133.00, 137.72, 137.74, 137.80, 138.88, 139.4, 139.5, 168.86, 168.89, 168.97. IR (KBr): 1741 and 1726 (C=O), 1436, 1241, 1221, 1130, 773, 702 cm^{-1}. Analysis calcd. for $C_{46}H_{34}O_8$: C, 77.30; H, 4.79. Found: C, 77.33; H, 5.00.

Dimethyl 4,4′-biphenylenebis(4-phenyl-1-naphthalene-2,3-dicarboxylate), 7c

Difuran **3c** (0.30 g, 0.56 mmol) and 240 mg DMAD (1.7 mmol) were refluxed in 150 mL dioxane for 8 h. The solvent was removed by rotary evaporation and evacuation under high vacuum. Acetonitrile (30 mL) and sodium iodide (0.54 g, 3.4 mmol) were added, the flask purged with nitrogen, and cooled to 0 °C. Chlorotrimethylsilane (0.50 mL, 3.9 mmol) was added by syringe and the reaction stirred for 6 h. The mixture was filtered and the solid material recrystallized from $CHCl_3$/MeOH to give 246 mg of **7c**, (57%): mp 368–370 °C. ^{1}H NMR (250 MHz, $CDCl_3$) δ: 3.54 (s, 6H), 3.60 (s, 6H), 7.40–7.55 (m, 18H), 7.68–7.79 (m, 4H), 7.87 (d, *J* = 7 Hz, 4H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ: 52.4, 52.6, 126.9, 127.6, 127.7, 127.96, 127.98, 128.1, 128.3, 129.0, 130.2, 130.8, 133.0, 137.1, 137.8, 138.9, 139.4, 140.1, 169.0. IR (Nujol): 1742, 1227, 1163, 1130, 774, 721, 700 cm^{-1}. MS (EI) *m/e*: 790 (M$^+$, 22), 744 (5), 552 (21), 457 (44), 456 (100), 207 (20), 126 (9), 78 (11).

Acknowledgements

The authors wish to thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and the University of Lethbridge for funding (RTB and PWD) and the Centre for Molecular Architecture, Central Queensland, Australia for analytical support.

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