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Naphtho[1,2-*c*:5,6-*c*]difuran: A Reactive Linker and Cyclophane Precursor

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Naphtho[1,2-*c*:5,6-*c*]difuran has been isolated in a 9-step synthesis from 2,6-dimethylnaphthalene. It is a highly reactive diene similar in nature to the related isobenzofuran. In Diels−Alder reactions, its intermediate monoadducts are actually less reactive that the parent difuran making possible sequential Diels−Alder reactions with different dienophiles. Reaction with a tethered bis(dienophile) leads to the production of a naphthalenic cyclophane.

The chemistry of isobenzofuran (IBF, **1,** Figure 1) and related compounds is of great interest and has been reviewed on a regular basis.[1−5] The commercially available diphenylisobenzofuran is used as a trap for reactive olefins,[6,7] as a singlet oxygen scavenger,[8] and for a host of other applications. Isobenzofurans are also of considerable theoretical interest and have found application as intermediates in the synthesis of various natural products.[2] Much of the utility of isobenzofurans lies in their substantial reactivity in Diels−Alder reactions. Recently, we have been interested in the preparation of molecules which contain two IBF moieties linked by a phenyl or biphenyl ring. In an earlier communication[9] we reported the synthesis of naphtho[1,2-*c*:5,6-*c*]difuran, **2**, and we now wish to give the full experimental details of its synthesis and some new results associated with its reactivity.

In our earlier work involving the synthesis of related naphtho[1,2-*c*]furan, **3**, we generated the furan ring via metal−halogen exchange of an *o*-bromobenzyl alcohol followed by reaction with DMF.[10] The resulting hemiacetal served as a precursor to the furan under conditions of acid catalysis or could be converted into an acetal that gave the furan with use of Rickborn's base-induced protocol.[11] Applying the same approach to the synthesis of **2** required the preparation of dibromodiol **4** (Scheme 1). This synthesis was achieved by electrophilic bromination of 2,6-dimethylnaphthalene followed by radical bromination of the methyl groups. Hydrolysis gave the dibromodiol **4**. Attempts to dimetalate **4** with excess *n*-butyllithium failed. The starting material is not very soluble even before deprotonation by the first two equivalents of butyllithium and the subsequent metal−halogen exchange would give a species with a significant amount of negative charge that may not be well-accommodated. In any event, decomposition appeared to be the result of attempts to metalate **4** since starting material was not recovered.

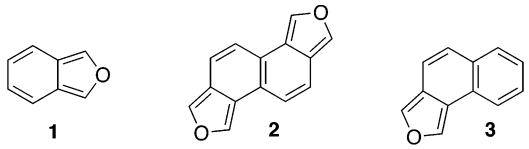

FIGURE 1. Isobenzofuran (**1**), naphtho[1,2-*c*:5,6-*c*]difuran (**2**), and naphtho[1,2-*c*]furan (**3**).

Protection of the alcohols as *tert*-butyldimethylsilyl ethers followed by metalation fared no better, decomposition being the problem again. We chose to oxidize the alcohols to aldehydes, protect as acetals, and subsequently metalate to eliminate the difficulty of charge buildup. This procedure worked well despite the poor solubility of dibromobis(acetal) **8** in the metalation reaction. Reduction of the aldehydes followed by cyclization gave bis(acetal) **11** as a mixture of syn and anti diastereomers.

Treatment of bis(acetal) **11** with excess LDA in ether afforded difuran **2**. Unlike isobenzofuran, it is a fairly stable solid at room temperature and could be chromatographed on alumina. Its NMR spectrum consists of two doublets for the furan protons (J = 1.6 Hz) and an AB quartet for the protons of the carbocyclic ring. The

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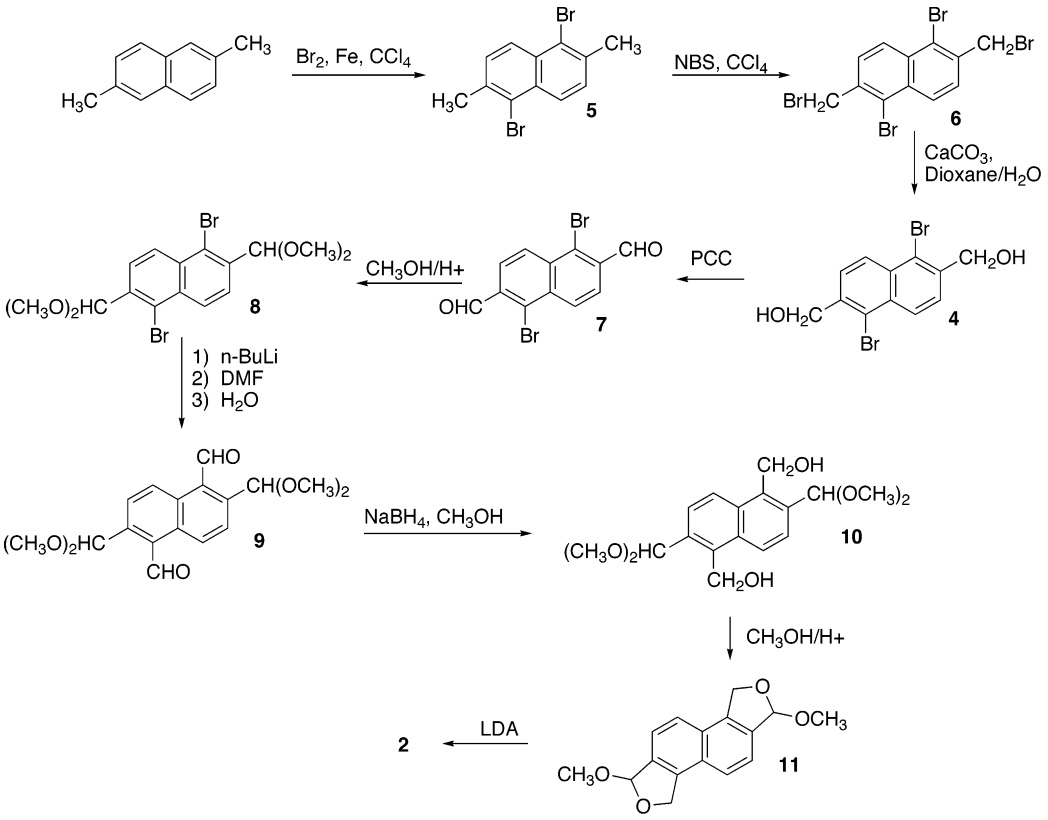
SCHEME 1



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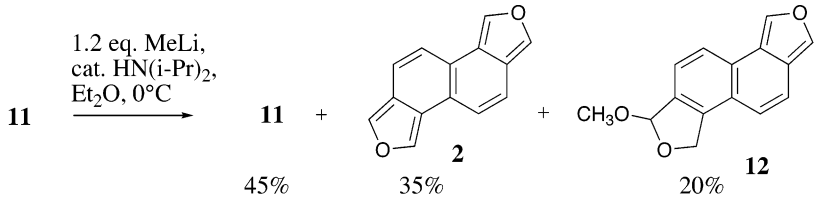

coupling constant in the AB system of 9.3 Hz indicates a high degree of double bond character in this bond, and is very similar to the 9.2-Hz coupling observed in **1**.[12] This observation is consistent with the picture of **1** and **2** as being mainly polyene in character.

Acetal **11** was treated with a single equivalent of LDA (Scheme 2) in an effort to selectively eliminate only one of the two methoxy groups to explore the possibility of stepwise formation and trapping of the two furan moieties. Both eliminations involve a significant loss of resonance energy associated with the naphthalenic ring. The first elimination involves the loss of only four electrons worth of resonance energy, the second, six. There was some hope, therefore, that the first elimination might take place significantly faster than the second. The result of this experiment was a mixture of starting material, difuran **2**, and the monoelimination product **12** in a ratio of about 2:2:1. The proportions of **2** and **12** suggest that, despite the fact that in the former case the reactant sacrifices slightly more resonance energy, it is the second elimination that is faster. We have seen a similar example of this phenomenon since doing this experiment. While performing a competition experiment between phenanthro[2,3-*c*]furan and isobenzofuran,[13] both species were formed simultaneously by treating a mixture of their acetal precursors with LDA. NMR spectra obtained before elimination is complete show that phenanthro[2,3-*c*]furan forms more readily than IBF despite the fact that the former product sacrifices slightly more resonance energy. This outcome suggests that some factor, such as the acidity of the acetal CH_2, plays a significant role in the kinetics of elimination rather than thermodynamic considerations concerning loss of aromatic character.

Wege has examined the reactivity of isobenzofuran and its benzologues in great detail and has determined that their second-order rate constants give a linear Herndon relationship against a parameter known as the structure count ratio.[14] The application of this Herndon relationship to difurans has some interesting ramifications. Scheme 3 shows the stepwise reaction of **2** with 2 equiv of *N*-methylmaleimide, **13**, and gives the structure of the intermediate monoaddition adduct, **14**. Difuran **2** would

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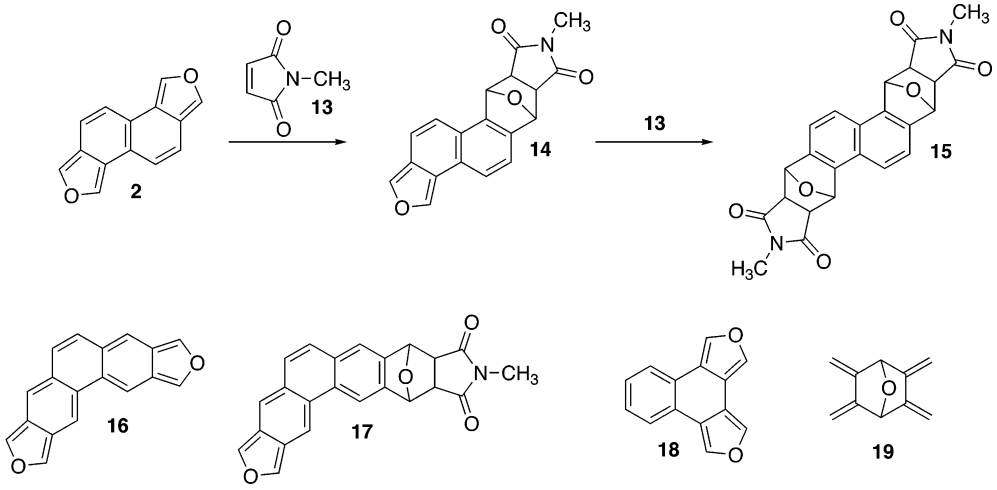
SCHEME 3



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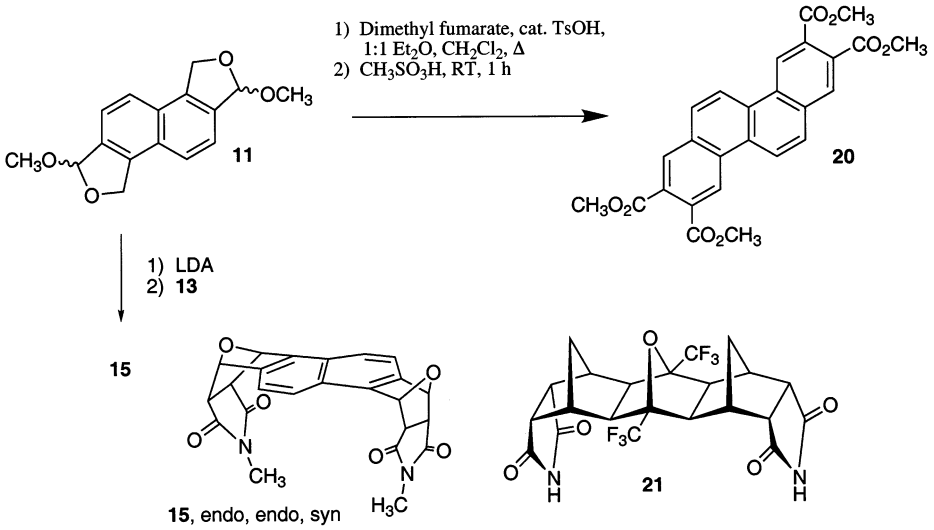

be expected to be comparable in reactivity to **1**. In the second reaction, however, intermediate **14** contains the substructure of naphtho[1,2-*c*]furan (**3**). The parent hydrocarbon is a known compound[15,16] and Wege has shown it to be 40 times less reactive than IBF itself. On this basis, one might predict that reaction of **2** with a single equivalent of **13** should give intermediate **14** fairly cleanly and that it would be sufficiently stable to be isolated. This experiment is somewhat akin to a competition experiment in that during the course of reaction, reactant **2** and product **14** (once its concentration builds) will compete for **13** as it is added. Upon performing this experiment, intermediate **14** was indeed the only observable product formed. Given the results of this experiment, it seems very likely that it will be possible to trap difuran **2** with two different dienophiles, something that would be quite useful.

In the case described above, Wege's data accurately predict the reactant to be more reactive than the intermediate. It is worth pointing out that this is not the case for all benzodifurans. We are currently working on a synthesis of phenanthrodifuran **16**. In this example, the difuran should be as reactive as **1**, but the intermediate **17** has the substructure of the more reactive benzologue phenanthro[2,3-*c*]furan.[13] Therefore, in the case of **16**, the second Diels−Alder reaction should be faster than the first, opposite to the case of **2**. This should also be true for a known isomer of **2**:[16] naphtho[1,2-*c*:3,4-*c*]difuran **18** should have reactivity comparable to that of furan. Its monoaddition product, however, has **3** as a substructure and should be much more reactive than **18**. Details of its reactivity have not been published. Sequential diene reactivity similar to ours has been reported for diene **19**.[17]

Diels−Alder adducts of **2** could be prepared in two ways (Scheme 4). A mixture of acetal **11** and excess dimethyl fumarate in the presence of TsOH gave the bis(fumarate) adduct as a complex mixture of syn and anti diastereomers. Presumably, this adduct is formed via stepwise Diels−Alder reactions via a monofuran intermediate rather than by the intermediacy of **2** itself. The adduct was smoothly aromatized to chrysene **20** upon treatment with methanesulfonic acid, demonstrating that

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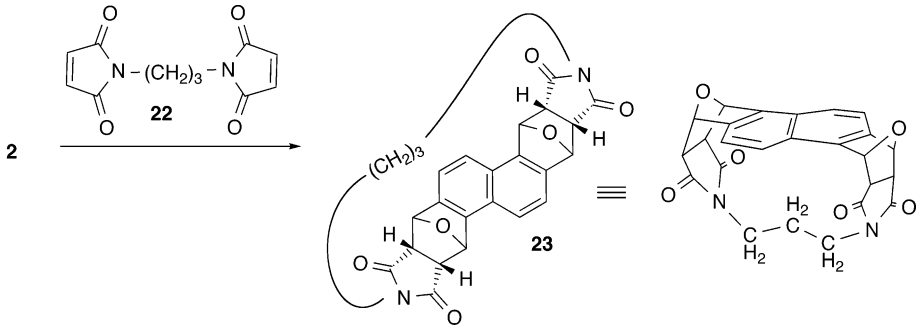
SCHEME 5



2 is a useful precursor to substituted chrysene derivatives. Alternatively, **2** can be generated with LDA and subsequently treated with a dienophile. This was done by using **13** as the dienophile giving **15**, again as a mixture of syn and anti diastereomers, exclusively endo.

The endo, endo, syn diastereomer of adduct **15** bears a topological similarity to molecular rack **21** reported by Warrener.[18−20] Warrener has shown that it is possible to tether various carbon chains, with and without functional groups, between the two nitrogen atoms (6 Å apart) to form alicyclophanes. In a recent paper, an isobenzofuran was tethered on a rack and was found to be markedly more stable.[20] To make a comparable tethered naphthalenic cyclophane from **2** requires the use of tethered bis(dienophile)s to obtain exclusively the desired endo, endo, syn product. Based on Warrener's racks, the N−N bond distance of 5.7 Å in **15** (determined by AM1 modeling) suggested that two maleimides tethered by three methylene units (**22** Scheme 5) would be suitable for the formation of a cyclophane, **23**. The other likely outcome of this reaction is the formation of polymer. A similar reaction using a bis(isobenzofuran) to prepare a cyclophane has been reported.[21]

Our first attempt at the preparation of **23** was performed under acid-catalyzed conditions. A mixture of **11** and tethered dienophile **22** was refluxed in diethyl ether in the presence of TsOH. An NMR spectrum of the crude reaction mixture indicated a mixture of polymer and **23** in a ratio of 3:2. The presence of **23** was indicated by sharp doublets corresponding to the bridgehead protons as opposed to broad signals for polymeric or oligomeric products. Unmistakable, however, was the appearance of the middle CH_2 of the tether as a multiplet at −1.4 ppm. AM1 models of **23** show that the tether is locked into a staggered conformation such that the protons of the middle CH_2 are pointing directly into the shielding region of the naphthalenic ring. This upfield multiplet is unmistakable evidence for the formation of **23**. AM1 models of **23** have an N−N bond distance of 4.9 Å, slightly shorter than the distance of 5.7 Å in the untethered **15**. There is a slight warp to the naphthalene ring and small distortions in the bridged rings to accommodate this strain.

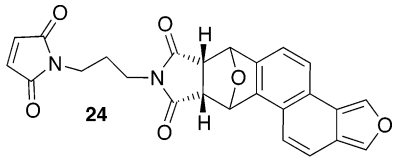


FIGURE 2. Intermediate in the formation of **23**.

We have found that the best way to maximize the production of cyclophane over polymer is to add a dilute solution of difuran **2** to a dilute solution of **22** at −40 °C. When the reaction is performed in this way, one can obtain the cyclophane in better yield (29%) with very little evidence of polymer in the crude NMR spectrum of the reaction mixture.

In the desired reaction, endo intermediate **24** (Figure 2) must undergo intramolecular Diels−Alder reaction to form the cyclophane. Intermolecular reaction of **24** with **2**, **22**, or itself leads to polymer. In the two sequential Diels−Alder reactions, the first (between **2** and **22**) involves the more reactive diene as discussed above. The second reaction, while involving a less reactive diene, is intramolecular. In an effort to determine whether the first Diels−Alder reaction is faster than the second, we tried to obtain a proton NMR spectrum of intermediate **24** by mixing solutions of **2** and **22** at −80 °C in methylene chloride-d_2 followed by data acquisition in a cold probe. Only signals of **23** were observed, indicating that both reactions are fast, even at −80 °C.

At this point, we have established some interesting features in the reactivity of naphtho[1,2-*c*:5,6-*c*]difuran and shown that it can be used to prepare chrysene derivatives and cyclophanes that are comparable to tethered molecular racks. We are in the process of preparing several more cyclophanes to see what tether lengths can be accommodated and what functional groups might be incorporated. While there is clear evidence of polymer formation in the reactions of **2** with bis(dienophile)s, we have not attempted to isolate or characterize any of these materials. Similar polymers have been reported and the potential utility of **2** has been mentioned in this context.[22]

Experimental Section

Solvents were used without additional purification with the exception of diethyl ether and THF, both of which were distilled from sodium metal prior to use. Melting points were

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performed in open capillaries and are uncorrected. The absence of ^{13}C data or missing ^{13}C signals is due to poor solubility. Molecular modeling calculations (MM+ and MNDO) were performed with HyperChem release 4.5, Hypercube, Inc., Waterloo, Ontario, N2L 3X2, Canada. Complex ^1H NMR coupling patterns for **23** were simulated by using MestRe-C[23] to determine the coupling constants.

1,5-Dibromo-2,6-bis(bromomethyl)naphthalene, 6. Dibromide **5** (7.3 g, 23 mmol) and *N*-bromosuccinimide (12.6 g, 71 mmol) were brought to reflux in 200 mL of carbon tetrachloride. A small amount of benzoyl peroxide was added and, after 1.5 h, another portion of benzoyl peroxide was added. Refluxing was continued for a total of 4 h. The mixture was cooled, saturated $NaHCO_3$ solution (200 mL) was added, and the mixture was filtered giving a white solid that was then air-dried to give 7.0 g (64%) of **6**, which was used without further purification. An analytical sample obtained by recrystallization from toluene/hexanes gave the following: mp 255−259 °C; ^1H NMR (250 MHz, $CDCl_3$/DMSO-d_6) δ 4.95 (s, 4H), 7.83 (d, J = 10 Hz, 2H), 8.33 (d, J = 10 Hz, 2H); IR (KBr) 1312, 1222, 1205, 1149, 819, 728, 699 cm^{-1}; MS (EI) *m/e* calcd for $C_{12}H_8Br_4$ 467.7362, found 467.7358; 472 (M + 4, 25), 470 (M + 2, 15), 468 (M^+, 5), 395 (33), 393 (100), 391 (100), 389 (35), 314 (34), 312 (65), 310 (35), 233 (12), 152 (43).

Anal. Calcd for $C_{12}H_8Br_4$: C, 30.81; H, 1.72. Found: C, 30.52; H, 1.90.

1,5-Dibromo-2,6-naphthalenedimethanol, 4. Tetrabromide **6** (6.7 g, 14 mmol) was stirred in 200 mL of dioxane. A slurry of 31 g (31 mmol) of $CaCO_3$ in 100 mL of water was added and the mixture refluxed for 48 h. The dioxane was removed by rotary evaporation and the residue treated with 6 M HCl until acidic. A white solid was filtered from the mixture, washed well with water, and air-dried to give 4.72 g (96%) of crude **4**, which was used without purification. An analytical sample was obtained from THF, which had mp 260−264 °C; ^1H NMR (250 MHz, $CDCl_3$/DMSO-d_6) δ 4.79 (d, J = 6 Hz, 4H), 5.58 (t, J = 6 Hz, 2H), 7.85 (d, J = 9 Hz, 2H), 8.29 (d, J = 9 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/DMSO-d_6) δ 61.8, 118.7, 124.2, 125.1, 130.1, 138.4; IR (KBr) 3254, 1482, 1208, 1064, 809, 729 cm^{-1}; MS (EI) *m/e* calcd for $C_{12}H_{10}Br_2O_2$ 343.9049, found 343.9039; 348 (20), 346 (M^+, 39), 344 (23), 237 (12), 235 (12), 139 (17), 129 (29), 128 (100), 127 (28), 126 (23).

Anal. Calcd for $C_{12}H_{10}Br_2O_2$: C, 41.91; H, 2.93. Found: C, 41.86; H, 2.78.

1,5-Dibromo-2,6-naphthalenedialdehyde, 7. To a slurry of 9 g of crushed molecular sieves and 7.5 g (35 mmol) of PCC in 250 mL of methylene chloride was added 3.0 g (8.7 mmol) of diol **4**. The solution was brought to reflux for 4 h. After cooling, an equal volume of diethyl ether was added and the mixture was filtered through 8 cm of silica gel. The silica gel was washed with 8 200-mL portions of hot chloroform. The solution was stripped of solvent, and the residue was recrystallized from chloroform to give 2.0 g (67%) of dialdehyde **7**: mp 245−249 °C dec; ^1H NMR (250 MHz, $CDCl_3$) δ 8.12 (d, J = 8 Hz, 2H), 8.61 (d, J = 8 Hz, 2H), 10.69 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/DMSO-d_6) δ 125.0, 127.0, 132.5, 134.4, 190.6; IR (KBr) 1683, 1297, 1213, 935, 820, 765 cm^{-1}; MS (EI) *m/e* 344 (M + 4, 50), 343 (36), 342 (M + 2, 100), 341 (51), 340 (51, M^+), 313 (11), 204 (27), 126 (32), 125 (27), 124 (28), 74 (28).

Anal. Calcd for $C_{12}H_6Br_2O_2$: C, 42.15; H, 1.77. Found: C, 42.30; H, 1.75.

1,5-Dibromo-2,6-bis(dimethoxymethyl)naphthalene, 8. Dialdehyde **7** (2.0 g, 5.8 mmol) was refluxed for 10 h in 125 mL of methanol and 15 mL of trimethylorthoformate with a catalytic amount of PPTS. A white solid was obtained from methanol, 2.4 g (95%): mp 183−185 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 3.44 (s, 12H), 5.86 (s, 2H), 7.83 (d, J = 9 Hz, 2H), 8.41 (d, J = 9 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 54.4, 104.0, 123.7, 126.5, 127.5, 133.5, 136.8; IR (KBr) 1307, 1141, 1112, 1064, 1054, 961, 827, 709 cm^{-1}; MS (EI) *m/e* 436 (M + 4, 11), 434 (M + 2, 22), 432 (M^+, 11), 405 (46), 403 (97), 401 (45), 359 (21), 357 (48), 355 (21), 75 (54).

Anal. Calcd for $C_{16}H_{18}Br_2O_4$: C, 44.27; H, 4.18. Found: C, 44.40; H, 4.29.

2,6-Bis(dimethoxymethyl)-1,5-naphthalenedicarboxaldehyde, 9. Bis(acetal) **8** (1.26 g, 2,9 mmol) was added to 200 mL of dry diethyl ether and the slurry cooled to −80 °C under nitrogen. *n*-Butyllithium (2.5 mL of a 2.5 M solution, 6.3 mmol) was added, the solution swas tirred for 5 min and then warmed to 0 °C for 40 min. A small aliquot quenched with water had the following proton NMR spectrum: 3.38 (s, 12H), 5.55 (s, 2H), 7.57 (d, J = 8 Hz, 2H), 7.87 (d, J = 8 Hz, 2H), 7.92 (s, 2H), idicating complete metalation. DMF (0.7 mL, 10 mmol) was added and the mixture was stirred for 10 h. Water (50 mL) was added, the ether phase was separated, dried over $MgSO_4$, and filtered, and the solvent was removed. The residue was recrystallized from diethyl ether to give 0.83 g (86%) of **8**: mp 132−133 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 3.40 (s, 12H), 5.91 (s, 2H), 7.89 (d, J = 9 Hz, 2H), 8.98 (d, J = 9 Hz, 2H), 10.92 (s, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 53.9, 102.1, 126.9, 130.5, 130.8, 140.5, 194.0; IR (KBr) 1698, 1351, 1104, 1071, 912, 843 cm^{-1}; MS (EI) *m/e* calcd for $C_{18}H_{20}O_6$ 332.1260, found 332.1263; 332 (M^+, 10), 302 (10), 301 (55), 300 (100), 286 (17), 285 (88), 255 (17), 225 (27).

Anal. Calcd for $C_{18}H_{20}O_6$: C, 65.10; H, 6.07. Found: C, 64.89; H, 6.26.

2,6-Bis(dimethoxymethyl)-1,5-naphthalenedimethanol, 10. Dialdehyde **9** (1.25 g, 3.8 mmol) was stirred in 100 mL of methanol. Sodium borohydride (0.6 g, 16 mmol) was added and the mixture was stirred for 4 h. The reaction was then heated until homogeneous, cooled, and filtered to give 0.83 g of **10**. The filtrate was stripped of solvent and the residue recrystallized from methanol to give an additional 0.36 g of product (total yield 95%): mp 195−197 °C; ^1H NMR (250 MHz, $CDCl_3$) δ 2.52 (t, J = 7 Hz, 2H), 3.42 (s, 12H), 5.21 (d, J = 7 Hz, 4H), 5.76 (s, 2H), 7.77 (d, J = 9 Hz, 2H), 8.34 (d, J = 9 Hz, 2H); ^{13}C NMR (62.5 MHz, $CDCl_3$/DMSO-d_6) δ 52.6, 55.3, 100.9, 123.5, 123.8, 131.9, 133.1, 134.3; IR (KBr) 3412, 1356, 1113, 1065, 1018, 956 cm^{-1}; MS (EI) *m/e* calcd for $C_{18}H_{24}O_6$ 336.1573, found 336.1577; 336 (M^+, 23), 305 (29), 304 (55), 273 (100), 272 (47), 241 (84), 182 (20), 105 (24).

Anal. Calcd for $C_{18}H_{24}O_6$: C, 64.31; H, 7.20. Found: C, 64.12; H, 7.34.

3,8-Dimethoxy-1,3,6,7-tetrahydronaphtho[1,2-*c*:5,6-*c*]difuran, 11. In 30 mL of methanol were refluxed 0.54 g of **10** and a catalytic amount of PPTS for 10 h. Methanol was added at reflux until the solution was homogeneous. After cooling, a white solid was collected by filtration that proved to be **11**, 0.37 g (84%): ^1H NMR (250 MHz, $CDCl_3$) δ 3.47 (S, 6H), 5.46 and 5.61 (AB of ABX, J_{AB} = 13 Hz, J_{AX} = 0 Hz, J_{BX} = 2.5 Hz, 4H), 6.40 (d, J = 2.5 Hz, 2H), 7.56 and 7.67 (AB, J = 9 Hz, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 54.5, 72.6, 108.9, 121.6, 124.8, 128.0, 135.1, 137.8; IR (KBr) 1383, 1087, 1042, 1001, 958, 805 cm^{-1}; MS (EI) *m/e* calcd for $C_{16}H_{16}O_4$ 272.1049, found 272.1046; 272 (M^+, 20), 271 (11), 242 (15), 241 (100), 210 (9), 182 (24), 153 (15), 152 (15).

Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.63; H, 5.93. Found: C, 70.38; H, 6.00.

2,3,8,9-Chrysenetetracarboxylic Acid, Tetramethyl Ester, 20. Bis(acetal) **11** (100 mg, 0.37 mmol) and dimethyl fumarate (112 mg, 0.78 mmol) were dissolved in 40 mL of 1:1 diethyl ether/methylene chloride. A catalytic amount of TsOH was added and the solution refluxed for 4 h. The solvent was removed and the residue dissolved in 10 mL of methanesulfonic acid. After the mixture was stirred for 1 h, water was added and a solid product was collected by filtration. Recrystallization from methanol gave 109 mg of chrysene **20** (64%): mp 265−266 °C; R_f 0.38 (5% MeOH in CH_2Cl_2); ^1H NMR (250 MHz, $CDCl_3$) δ 4.02 (s, 6H), 4.04 (s, 6H), 8.14 (d, J = 9 Hz, 2H), 8.41 (s, 2H), 8.88 (d, J = 9 Hz, 2H), 9.18 (s, 2H); IR (KBr)

(23) Cobas, C.; Cruces, J.; Sardina, F. J. *MestRe-C Magnetic Resonance Companion*, version 2.3a; Universidad de Santiago de Compostela, 2000.

1723 (C=O), 1298, 1273, 1222, 1133 cm^{-1}; MS (EI) *m/e* calcd for $C_{26}H_{20}O_8$ 460.1158, found 460.1162; 460 (M^+, 100), 430 (30), 429 (75), 383 (8), 266 (7), 200 (10), 199 (39).

Anal. Calcd for $C_{26}H_{20}O_8$: C, 67.87; H, 4.38. Found: C, 68.07; H, 4.06.

Naphtho[1,2-*c*:5,6-*c*]difuran, 2. A suspension of 0.205 g (0.75 mmol) of **11** in 100 mL of dry ether was cooled to 0 °C under N_2. Diisopropylamine (20 μL) was added followed by 3.0 mL of 1.0 M MeLi (3 mmol). After 0.5 h, the reaction was quenched with water and sufficient ether added to dissolve all material. The ether layer was separated, dried over $MgSO_4$, and filtered. Approximately 5 g of neutral alumina was added and the solvent removed by rotary evaporation. The alumina/difuran was added to the top of a column of neutral alumina and eluted with 3% EtOAc/pet ether graded to 8%. The progress of elution of the difuran was monitored by shining long-range UV light on the column—the difuran fluoresces blue. Removal of the eluant gave 0.10 g of the difuran, 64%: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.37 and 7.41 (ABq, J = 9.2 Hz, 4H), 8.02 (d, J = 1.5 Hz, 2H), 8.25 (d, J = 1.5 Hz, 2H); ^{13}C NMR (62.5 MHz, acetone-d_6) δ 119.4 (d, J = 65 Hz), 122.7 (s), 123.1 (d, J = 61 Hz), 123.8 (s), 123.9 (s), 136.3 (dd, J = 5.8, 206 Hz), 137.7 (dd, J = 5.8, 206 Hz); IR (KBr) 1044, 851, 805, 753 cm^{-1}; UV–vis (*c* 3.8 × 10^{-5}, cyclohexane) λ_{max} 228 (4.4), 235 (4.5), 245 (4.4), 253 (4.3), 335 (3.3), 352 (3.6), 371 (3.9), 391 (4.0) nm; MS (EI) *m/e* calcd for $C_{14}H_8O_2$ 208.05243, found 208.05245; 208.05245 (M^+, 100), 180.05701 (15), 179.04961 (9), 152.01679 (22), 151.05412 (26), 150.04666 (18), 104.02605 (17), 75.02340 (8).

Syn and Anti Adducts of 2 with *N*-Methyl Maleimide: *N*,*N*′-Dimethyl 1,4,7,10-Diepoxy-1,2,3,4,7,8,9,10-octahydro-2,3,8,9-chrysenetetracarboxylic Acid, Diimide, 15. Acetal **11** (50 mg, 0.18 mmol) was dissolved in 30 mL of dry ether under nitrogen and cooled to 0 °C. LDA (1 mL of 2.0 M, 2 mmol) was added and the reaction stirred for 30 min. Water was added and the ether phase was isolated. The ether phase was added to a solution of *N*-methyl maleimide (55 mg, 0.50 mmol) in 25 mL of THF. The reaction was stirred overnight, taken up in methylene chloride, and washed with brine. The solution was dried with $MgSO_4$ and filtered and the residue was recrystallized from methanol to give 55 mg (70%) of **15** as a 1:1 mixture of diastereomers: mp >360 °C; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.95 (s, 3 H), 2.06 (s, 3 H), 3.76–3.82 (m, 4H), 5.76–5.81 (m, 2H), 6.05–6.11 (m, 2H), 7.17–7.76 (m, 4H); IR (KBr) 1773 and 1697, 1434, 1296, 1131, 865 cm^{-1}; MS (EI) *m/e* calcd for $C_{24}H_{18}N_2O_6$ 430.1165, found 430.1168; 430 (M^+, 1), 319 (12), 208 (100), 209 (17), 111 (5), 69 (10), 55 (11).

Monoadduct of 2 and *N*-Methyl Maleimide, 14. Acetal **11** (100 mg, 36 mmol) in 50 mL of THF was cooled to −70 °C under nitrogen. LDA (1.2 mL of a 2.0 M solution, 1.2 mmol) was added by syringe and the reaction was stirred for 30 min. An equal volume of water was added and the THF was removed by rotary evaporation. The residue was extracted with diethyl ether to a total volume of 75 mL. To this solution was added 41 mg of *N*-methyl maleimide (0.36 mmol) in 3 mL of THF in a dropwise manner. After the mixture was stirred for 1 h, the reaction was stripped, taken up in diethyl ether, dried over $MgSO_4$, and filtered. After removal of the solvent, the residue was recrystallized from diethyl ether, giving 52 mg (44%) of monoadduct **14**: mp 195 °C dec; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.06 (s, 3H), 3.76 (m, 2H), 5.74 (d, 1H), 6.03 (d, 1H), 7.06 (d, J = 10 Hz, 1H), 7.27 (d, J = 8 Hz, 1H), 7.28 (dd, J = 1, 9 Hz, 1H), 7.77 (dd, J = 1, 8 Hz, 1H), 7.86 (d, J = 1.5 Hz, 1H), 8.17 (dd, J = 1, 1.5 Hz, 1H); IR (KBr) 1771 and 1701, 1435, 1283, 1130, 969, 869 cm^{-1}; MS (EI) *m/e* calcd for $C_{19}H_{13}NO_4$ 319.0845, found 319.08361; 319 (M^+, 19), 209 (16), 208 (100), 152 (9), 151 (10), 104 (15), 87 (6).

3-Carbon Cyclophane 23. Acetal precursor **11** (263 mg, 0.966 mmol) was dissolved in 40 mL of dry diethyl ether and cooled to 0 °C under nitrogen. LDA (5.0 mL of a 2.0 M solution in heptane/THF/ethylbenzene, 10.0 mmol) was added via syringe and the mixture was stirred for 30 min. The reaction was quenched with water and extracted several times with ether. The combined ether extracts were washed once with brine, dried with $MgSO_4$, and filtered. Meanwhile, a solution of 228 mg (0.973 mmol) of the 3C tethered bismaleimide **22** in ~250 mL of THF was cooled to −40 °C. The difuran solution was added dropwise to the bis(dienophile) solution at −40 °C and the reaction mixture was stirred overnight, warming to room temperature. The solvent was removed by using a rotary evaporator, and the product passed through an alumina column with $CHCl_3$. The $CHCl_3$ was removed and the product recrystallized from $CHCl_3$/hexanes to give 124 mg of **23** (29%): mp 225 °C dec; ^{1}H NMR (250 MHz, $CDCl_3$) δ −1.41 (AA′ of AA′MM′NN′, symmetrical m, $^2J_{AA'}$ = −12 Hz, $^3J_{AM}$ = $^3J_{AN'}$ = $^3J_{A'M'}$ = $^3J_{A'N}$ = 4.0 Hz, $^3J_{AM'}$ = $^3J_{AN}$ = $^3J_{A'N'}$ = $^3J_{A'M}$ = 13.0 Hz, 2H), 2.59 and 2.80 (MM′NN′ of AA′MM′NN′, symmetrical m, $^2J_{MM'}$ = $^2J_{NN'}$ = −12 Hz, $^3J_{AM}$ = $^3J_{AN'}$ = $^3J_{A'M'}$ = $^3J_{A'N}$ = 4.0 Hz, $^3J_{AM'}$ = $^3J_{AN}$ = $^3J_{A'N'}$ = $^3J_{A'M}$ = 13.0 Hz, 4H), 3.82 and 3.90 (AB of ABMN, dABq, $^3J_{AB}$ = 8.0 Hz, $^3J_{AN}$ = 5.5 Hz, $^3J_{BM}$ = 5.5 Hz, 4H), 5.90 (M of ABMN, d, $^3J_{BM}$ = 5.5 Hz, 2H), 6.21 (N of ABMN, d, $^3J_{AN}$ = 5.5 Hz, 2H), 7.55 and 7.74 (ABq, J = 8.0 Hz, 4H); ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 25.7, 35.0, 46.7, 49.6, 80.5, 81.6, 120.5, 125.4, 128.3, 138.8, 141.3, 173.27, 173.34; IR (KBr) 3005, 2949, 1776 and 1701 (C=O), 1458, 1396, 1344, 1220, 1128, 1040, 866; MS (EI) *m/e* calcd for $C_{25}H_{18}N_2O_6$ 442.1165, found 442.1165; 442 (M^+, 17), 209 (18), 208 (100), 152 (5), 151 (5), 110 (5), 57 (7), 55 (5).

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