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Electrophilic Transannular Cyclization of Octadehydrodibenzo[12]annulene Reexamined: Indication of the Formation of Both *anti*- and *syn*-Indenofluorenes

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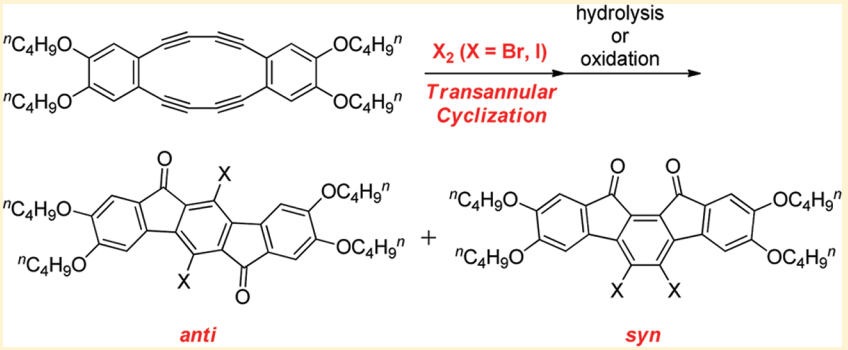
Supporting Information

ABSTRACT:



The reaction of tetrabutoxyoctadehydrodibenzo[12]annulene **2f** with iodine under aerobic conditions was reexamined. Contrary to previous reports, the present results revealed the formation of both *anti*-diiodoindenofluorenedione and its *syn* isomer through the oxidation of the respective tetraiodoindenofluorenes, indicating the occurrence of two modes of iodine-induced transannular cyclization. This was supported by the reaction of **2f** with bromine, which gave *anti*- and *syn*-hexabromodihydroindenofluorenes through interception of indenofluorene intermediates by bromine. The hexabromides were transformed into the corresponding dibromodiones by hydrolysis.

anti-Indenofluorene **1a**, systematically named indeno[1,2-*b*]-fluorene, is an attractive conjugated system in view of its physical properties (associated with its *p*-quinodimethane substructure embedded in the 20 π perimeter) and the potential optoelectronic applications. However, there have only been two reports on the synthesis and isolation of *anti*-indenofluorene derivatives. Swager et al. reported the first synthesis of air-sensitive tetraiodo derivatives **1b**−**e** by the iodine-induced transannular cyclization of the corresponding octadehydrodibenzo[12]annulenes ([12]DBAs: **2a**−**d**) under anaerobic conditions.[1] When carried out in the presence of oxygen, however, the same reaction of **2d** gave diiodoindenofluorenedione **3c**. Moreover, **1d** was readily oxidized to the corresponding *anti*-diketone **3b**.[1] Similarly, Komatsu et al. reported the formation of *anti*-indenofluorenedione **3d** through the treatment of perfluoro[12]DBA **2e** with iodine under oxygen.[2] Very recently, Haley et al. reported the synthesis of stable *anti*-indenofluorene derivatives **1f** and **1g** having four (triisopropylsilyl)ethynyl substituents,[3] which showed relatively small HOMO−LUMO gaps comparable to that of pentacene. Compounds **1f** and **1g** were derived from diiododiones **3a** and **3b**, respectively, which were obtained by the iodine-induced cyclization of the corresponding [12]DBAs **2a** and **2c**.

syn-Indenofluorene (systematic name: indeno[2,1-*a*]fluorene, **4a**), a conjugated hydrocarbon and a structural isomer of the *anti*-compound, has diminished stability owing to the *o*-quinodimethane substructure. Probably for this reason, *syn*-indenofluorene derivatives have been studied to an even lesser extent than have been the *anti*-isomers. More than five decades ago, Le Berre reported in a series of papers the isolation of the diphenyl derivative **4b** as an unstable violet solid that was easily oxidized by molecular oxygen.[4] These had been the only literature on the *syn*-indenofluorene system before our recent report on the isolation of the stable dimesityl derivative **4c** which was sterically protected by bulky substituents and the properties relevant to its singlet biradical character.[5]

In connection with our interest in the transannular cyclization of dehydrobenzoannulenes,[6] we reexamined the iodine-induced cyclization of [12]DBAs, which can be formulated by the mechanism shown in Scheme 1.[7] As per this mechanism, the initial electrophilic addition of iodine, accompanied by transannular bond formation between the two closely located acetylenic carbons, gives the bicyclo[7.3.0] ring system **5X**. The generation

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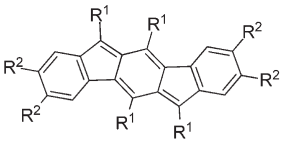
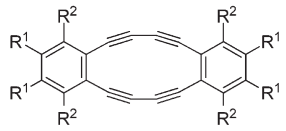
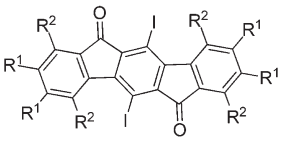


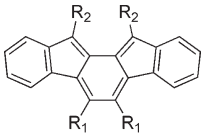
1a: $R^1 = R^2 = H$
1b: $R^1 = I$, $R^2 = H$
1c: $R^1 = I$, $R^2 = n\text{-}C_4H_9$
1d: $R^1 = I$, $R^2 = n\text{-}C_{10}H_{21}$
1e: $R^1 = I$, $R^2 = n\text{-}C_{12}H_{25}$
1f: $R^1 =$ ≡—TIPS, $R^2 = H$
1g: $R^1 =$ ≡—TIPS, $R^2 = n\text{-}C_{10}H_{21}$



2a: $R^1 = R^2 = H$
2b: $R^1 = n\text{-}C_4H_9$, $R^2 = H$
2c: $R^1 = n\text{-}C_{10}H_{21}$, $R^2 = H$
2d: $R^1 = n\text{-}C_{12}H_{25}$, $R^2 = H$
2e: $R^1 = R^2 = F$
2f: $R^1 = OC_4H_9{}^n$, $R^2 = H$



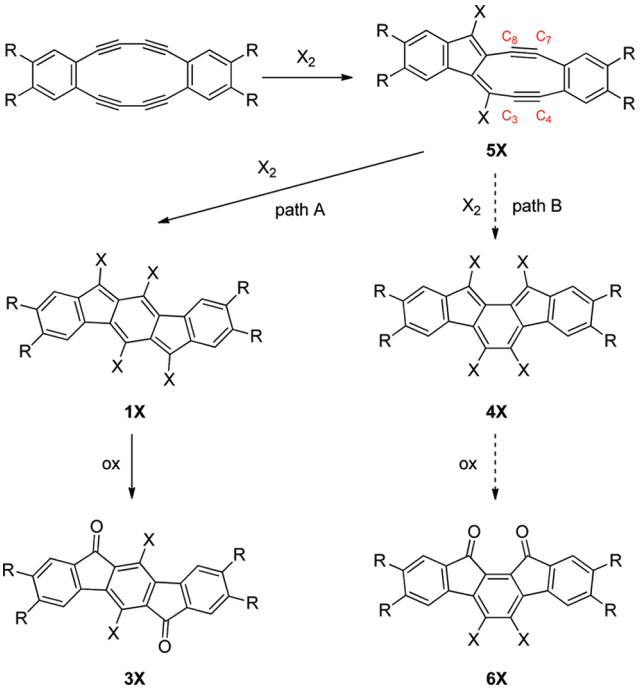
3a: $R^1 = R^2 = H$
3b: $R^1 = n\text{-}C_{10}H_{21}$, $R^2 = H$
3c: $R^1 = n\text{-}C_{12}H_{25}$, $R^2 = H$
3d: $R^1 = R^2 = F$
3e: $R^1 = OC_4H_9{}^n$, $R^2 = H$



4a: $R_1 = R_2 = H$
4b: $R_1 = H$, $R_2 = Ph$
4c: $R_1 = H$, $R_2 = Mes$

of a bicyclo[7.3.0] product via hydride-induced transannular bond formation of a 12-membered ring tetrayne has been reported previously.[8] The HOMO coefficients at C7 and C8 are larger than those at C3 and C4 of **5X** (Figure S11, Supporting Information), and the orbital energy gap between the HOMO and HOMO-1 energy levels of **5X** (0.60 eV for R = OMe, X = Br, and 0.60 eV for R = OMe and X = I) is relatively large, as calculated by the density functional theory (DFT) method at the B3LYP/6-31G*+LANL2DZ (for Br and I) level of theory.[9] Hence, in the second step, electrophilic attack of the halogen should occur at C7 or C8 rather than at C3 or C4 of **5X**. Therefore, there are two possible cyclization routes: (1) initial attack of an electrophile at C8, followed by transannular C3—C7 bond formation, to give the *anti*-indenofluorene product **1X** (path A), or (2) initial attack at C7, followed by C4—C8 bond formation, to afford *syn*-indenofluorene **4X** (path B). DFT calculations for the *anti*-isomers **1X**

Scheme 1. Transannular Bond Formation Pathways in the Reaction of [12]DBA with Halogens



and *syn*-isomers **4X** indicated that the former isomers are substantially more stable (7.43 kcal/mol for R = OMe, X = Br, and 4.53 kcal/mol for R = OMe, X = I).[9] In contrast, on the basis of the larger HOMO coefficients at C7 than those at C8 as well as the Mulliken charge distributions at C7 and C8 (Figure S11, Supporting Information), the initial addition of the halogen should occur at C7. The thermodynamic and kinetic considerations thus conflict. In the presence of oxygen, **1X** may be transformed into the diketone **3X**, as shown by Swager, whereas *syn*-indenofluorene **4X**, in view of the reported reactivity of the diphenyl derivative **4b**,[4] would probably decompose into a complex mixture of products including the dione **6X**. We considered that this must be why the *syn* products were not found in the reaction of [12]DBAs with iodine. In this context, we reexamined the reaction of [12]DBA **2f** with iodine to determine whether the *syn* product was indeed formed. Moreover, the use of bromine instead of iodine allowed the interception of the elusive indenofluorenes via the 1,6- and 1,4-additions of bromine, leading to the formation of both *anti*- and *syn*-hexabromodihydroindenofluorenes **7** and **8**, and thus providing circumstantial evidence for the occurrence of both modes of cyclization.

Tetrabutoxy[12]DBA **2f** was prepared by Eglinton coupling of dibutoxydiethynylbenzene, as reported previously.[6] First, we examined the reaction of DBA **2f** with iodine (Scheme 2). The reaction of DBA **2f** with iodine under an inert atmosphere gave *anti*-diiodoindenofluorenedione **3e** as a sparingly soluble solid: we were unable to isolate the expected *anti*-tetraiodoindenofluorene **1X** (X = I, R = $OC_4H_9{}^n$; Scheme 1), unlike the cases reported by Swager and Haley.[1,3] Considering the sensitivity of **1X** (X = I, R = alkyl groups) toward oxygen[1] together with the electron-donating property of the alkoxy substituents, it is reasonable to assume that alkoxy-substituted tetraiodoindenofluorene **1X** (X = I,

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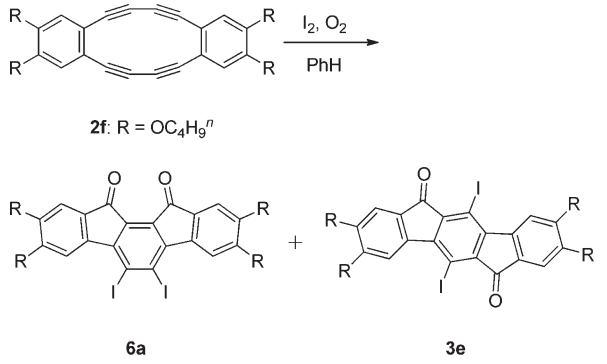
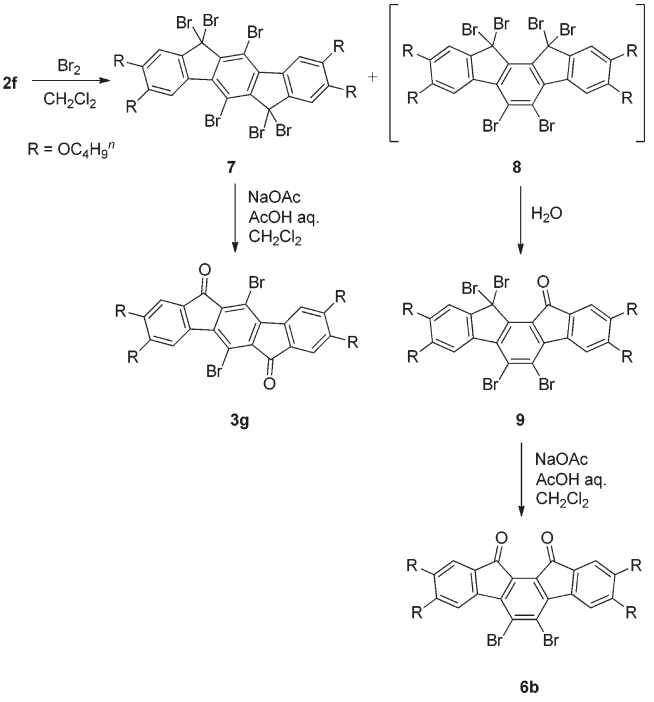
Scheme 2. Reaction of [12]DBA 2f with Iodine



Scheme 3. Reaction of [12]DBA 2f with Bromine



R = $OC_4H_9^n$; Scheme 1) is easily oxidized by residual oxygen during the reaction.[10] We also found a substantial amount of *syn*-diiiodoindenofluorenedione **6a** in the reaction mixture together with unidentified products by the ^{1}H NMR spectrum (Figure S1, Supporting Information). When the reaction was undertaken under an oxygen atmosphere, the reaction proceeded cleaner as shown in Figure S2 (Supporting Information). We isolated not only *anti*-product **3e** (58% yield) but also the *syn*-isomer **6a** in low yield (8%).[11] These results suggest that *syn*-indenofluorene **4X** (X = I, R = $OC_4H_9^n$; Scheme 1) must have been formed in the reaction of [12]DBA **2f** and then oxidized to give **6a**. However, because of the moderate total yield of the products, it is not possible to deduce the ratio of the products obtained through paths A and B.

Next, the reaction of **2f** with bromine was examined (Scheme 3). Treatment of **2f** with 4 equiv of bromine in CH_2Cl_2 under an argon atmosphere gave two compounds (assigned **7** and **8**) in a ratio of 1.0:1.7. As shown in Figure S3 (Supporting Information), the ^{1}H NMR spectrum of the crude product exhibited only two pairs of singlet peaks in the aromatic region and two OCH_2 signals. The ^{13}C NMR spectrum (Figure S3, Supporting Information) showed two groups of signals consisting of nine aromatic sp^2 peaks and one sp^3 carbon peak (at 52.0 and 48.9 ppm), respectively, in addition to those due to the butoxy groups. These results indicated the formation of two hexabromodihydroindenofluorene isomers. Indeed, one of the products (the minor product) isolated by preparative HPLC in 30% yield was characterized as *anti*-hexabromodihydroindenofluorene **7** on the basis of the spectroscopic data. The structure of **7** was further confirmed by X-ray crystallographic analysis (Figure S5, Supporting Information). However, during purification by HPLC, the other product was partially hydrolyzed to give the ketone **9**. When the same reaction was conducted under an oxygen atmosphere, in addition to **7** and **8**, *syn*-ketone **9** was detected by the ^{1}H NMR spectrum of the crude reaction mixture (Figure S4, Supporting Information). Though the formation mechanism of monoketone **9** is not understood, this result is consistent with the observed high reactivity of *syn*-indenofluorene **4X** (X = I, R = $OC_4H_9^n$; Scheme 1) toward oxygen. The ratio of the *syn*-products (**8** and **9**) and *anti*-product (**7**) is almost identical with that observed under an inert atmosphere. In contrast to the reaction with iodine under oxygen, however, diketones **3g** and **6b** were not obtained in the reaction of **2f** with bromine even under aerated conditions, since *anti*-tetrabromoindenofluorene **1X** (X = Br, R = $OC_4H_9^n$; Scheme 1) was trapped quickly with bromine via 1,6-addition before it reacted with oxygen.

The ^{1}H NMR and ^{13}C NMR spectra of **9** indicate that this is an unsymmetrical pentacyclic ketone: in the ^{13}C NMR spectrum, the carbonyl carbon resonates at 188.0 ppm. In the IR spectrum, the carbonyl absorption peak appears at 1712 cm^{-1}. On the basis of the spectroscopic data and the fact that **9** was further hydrolyzed to give the diketone **6b**, we deduced the structure of the major product of the bromination of **2f** to be *syn*-hexabromodihydroindenofluorene **8**.

The obtained *anti*-hexabromide **7** was also hydrolyzed under acidic conditions to give the corresponding *anti*-indenofluorenedione **3g**. Though the spectral properties of **3g** and **6b** were very similar to each other, the *anti*-indenofluorene backbone of **3g** was evident from the structure of its precursor **7**, whose structure was confirmed by X-ray crystallography. Therefore, it is reasonable to conclude that **6b** has a *syn*-indenofluorene framework.

The above results clearly show that both *anti*- and *syn*-indenofluorenes **1X** and **4X** (X = I or Br, R = $OC_4H_9^n$; Scheme 1) were formed by the halogen-induced transannular cyclization of [12]DBA **2f**. In the case of iodine-induced cyclization, because of the low reactivity of iodine toward electrophilic addition, **1X** and **4X** (X = I, R = $OC_4H_9^n$; Scheme 1) were oxidized under aerobic conditions before being intercepted by iodine. In previous studies, only *anti*-indenofluorenediones were isolated probably because of the high reactivity of *syn*-indenofluorene **4X** (X = I, R = $OC_4H_9^n$; Scheme 1) toward decomposition by reaction with molecular oxygen: this might have been the reason for the difference in the results obtained under subtly different reaction conditions and workup procedures. On the other hand, in the case of bromination, the reactive intermediates **1X** and **4X** (X = Br, R = $OC_4H_9^n$; Scheme 1) were intercepted by the 1,6- and 1,4-additions of bromine, respectively. The different preference in the mode of cyclization observed for the reaction with iodine and bromine can be ascribed to the subtle balance between kinetic and thermodynamic factors as described above. These results provide a useful insight

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into the synthesis of new aromatic ring systems that are otherwise difficult to obtain via multiple transannular cyclization processes of alkynes.

EXPERIMENTAL SECTION

General Methods. All reactions were performed under an inert atmosphere (nitrogen or argon) unless otherwise noted. Commercially available reagents and solvents were used as received except for the dry solvents. Dry benzene was prepared by distillation from CaH_2. Dry THF and CH_2Cl_2 were purchased and purified through a Glass Contour solvent system. Chemical shifts (δ) are expressed in ppm referred to the residual nondeuterated solvent as the internal standard ($CDCl_3$; ^1H 7.26 ppm, ^{13}C 77.0 ppm). GPC was performed using JAIGEL-1H and 2H GPC columns (600 mm × 20 mm) with $CHCl_3$ as the eluent. HPLC was performed using a Develosil C30-UG-5 column with a mixture of MeCN and CH_2Cl_2 as the eluent.

Synthesis of 1,2-Dibutoxy-4,5-bis[(trimethylsilyl)ethynyl]-benzene (10). To an argon-purged solution of 1,2-dibutoxy-4,5-diiodobenzene (**11**)[12] (2.97 g, 6.26 mmol) in Et_3N (40 mL) were added $Pd(PPh_3)_4$ (362 mg, 313 μmol) and CuI (119 mg, 626 μmol), followed by (trimethylsilyl)acetylene (2.7 mL, 19 mmol). The mixture was stirred at rt for 90 min. After evaporation of the solvent under reduced pressure, the crude product was subjected to silica gel column chromatography (hexane/$CHCl_3$ = 2/1) to give 1,2-dibutoxy-4,5-bis-[(trimethylsilyl)ethynyl]benzene (**10**) (2.02 g, 78%) as a white solid: mp 47−48 °C; ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 6.91 (s, 2H), 3.98 (t, J = 6.5 Hz, 4H), 1.79 (quint, J = 6.5 Hz, 4H), 1.55−1.43 (m, 4H), 0.97 (t, J = 7.5 Hz, 6H), 0.26 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 149.1, 118.8, 116.4, 103.6, 96.4, 68.8, 31.1, 19.2, 13.8, 0.1; IR (KBr) 2959, 2901, 2868, 2152, 1593, 1510, 1466, 1403, 1385, 1356, 1263, 1250, 1221, 1203, 1121, 1066, 1038, 1023, 1007, 970, 919, 895, 840, 758, 699, 641 cm^{-1}; HRMS (FAB) calcd for $C_{24}H_{38}O_2Si_2$ 414.2410 (M^+), found 414.2410. Anal. Calcd for $C_{24}H_{38}O_2Si_2$: C, 69.50; H, 9.24. Found: C, 69.49; H, 9.52.

Synthesis of 2,3,10,11-Tetrabutoxydibenzo-5,6,7,8,13,14,15,16-octadehydro[12]annulene (2f). To a solution of **10** (13.0 g, 31.3 mmol) in MeOH (100 mL) was added K_2CO_3 (17.3 g, 125 mmol). The mixture was stirred at rt for 8 h. After dilution with ether and water, the aqueous phase was separated and extracted with ether. The combined organic layers were washed with water and brine and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure gave the deprotected diethynylbenzene, which was used in the next reaction without further purification. A degassed solution of the terminal alkyne in pyridine (120 mL) and MeOH (120 mL) was added slowly to a degassed solution of $Cu(OAc)_2$ (34.2 g, 188 mmol) in pyridine (500 mL) at rt during overnight. After completion of the addition, the mixture was stirred at rt for 5.5 h. After dilution with CH_2Cl_2, the mixture was washed with aqueous 1 N HCl and brine and then dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the product was purified by silica gel column chromatography (hexane/CH_2Cl_2 = 1/1), followed by GPC, to give **2f** (1.50 g, 18%) as a yellow solid: mp 114−115 °C dec; ^1H NMR (300 MHz, $CDCl_3$, 30 °C) δ 6.40 (s, 4H), 3.87 (t, J = 6.6 Hz, 8H), 1.74 (quint, J = 6.6 Hz, 8H), 1.54−1.38 (m, 8H), 0.95 (t, J = 7.4 Hz, 12H); ^{13}C NMR (68 MHz, $CDCl_3$, 30 °C) δ 149.7, 123.8, 113.7, 92.2, 83.4, 69.0, 31.1, 19.2, 13.9; IR (KBr) 2956, 2871, 2183, 1592, 1548, 1494, 1464, 1440, 1393, 1317, 1270, 1202, 1183, 1065, 1026, 972, 863 cm^{-1}; HRMS (FAB) calcd for $C_{36}H_{41}O_4$ [(M + H)$^+$] 537.3005, found 537.2990. Anal. Calcd for $C_{36}H_{40}O_4$: C, 80.56; H, 7.51. Found: C, 80.57; H, 7.83.

Iodine-Induced Transannular Cyclization of 2f under an Oxygen Atmosphere: Formation of 2,3,8,9-Tetrabutoxy-5,11-diiodoindeno[1,2-*b*]fluorene-6,12-dione (3e) and 2,3,8,9-Tetrabutoxy-5,6-diiodoindeno[2,1-*a*]fluorene-11,12-dione (6a). To a mixture of [12]DBA **2f** (103 mg, 192 μmol) and iodine (614 mg, 2.42 mmol) was added oxygen-bubbled dry benzene (20 mL). The solution was stirred vigorously under oxygen at rt for 20 h. After dilution with $CHCl_3$ (~400 mL), the mixture was washed with a saturated aqueous solution of $Na_2S_2O_3$ and brine and then dried over $MgSO_4$. The solvent was evaporated, and the crude mixture was suspended in $CHCl_3$ (~5 mL) and filtered. The insoluble solid was washed with a small amount of $CHCl_3$ to give *anti*-diiododione **3e** (78.1 mg) as a dark green solid. The combined filtrate was subjected to silica gel column chromatography twice ($CHCl_3$ only and $CHCl_3$/AcOEt = 100/1) to give additional *anti*-diiododione **3e** (13.3 mg: total 91.4 mg, 58%) and *syn*-diiododione **6a** (13.0 mg, 8.2%) as an orange solid.

anti-Diiododione ***3e***: mp 269−270 °C; ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.59 (s, 2H), 7.21 (s, 2H), 4.20 (t, J = 6.5 Hz, 4H), 4.08 (t, J = 6.5 Hz, 4H), 1.93−1.78 (m, 8H), 1.59−1.48 (m, 8H), 1.02 (t, J = 7.5 Hz, 6H), 1.00 (t, J = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 50 °C) δ 189.3, 154.2, 150.4, 148.9, 139.0, 136.8, 127.4, 109.4, 108.5, 83.8, 69.5, 69.4, 31.22, 31.17, 19.3, 19.2, 13.81, 13.76; IR (KBr) 2956, 2930, 2870, 1707, 1583, 1503, 1466, 1444, 1418, 1372, 1322, 1269, 1243, 1208, 1110, 1063, 1018, 960, 870, 822, 807, 780, 675, 629, 553 cm^{-1}; HRMS (EI) calcd for $C_{36}H_{40}O_6I_2$ 822.0914 (M^+), found 822.0916.

syn-Diiododione ***6a***: mp 237−240 °C; ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.35 (s, 2H), 7.24 (s, 2H), 4.16 (t, J = 6.5 Hz, 4H), 4.08 (t, J = 6.5 Hz, 4H), 1.92−1.78 (m, 8H), 1.59−1.47 (m, 8H), 1.02 (t, J = 7.5 Hz, 6H), 1.00 (t, J = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 187.7, 153.3, 150.7, 146.8, 139.1, 134.1, 128.0, 110.9, 108.4, 107.7, 69.2, 69.0, 31.1, 19.3, 19.2, 13.9, 13.8; IR (KBr) 2956, 2932, 2871, 1718, 1573, 1490, 1464, 1355, 1332, 1276, 1211, 1106, 1065, 1038, 966, 896, 868, 784, 768, 628, 605, 583 cm^{-1}; HRMS (EI) calcd for $C_{36}H_{40}O_6I_2$ 822.0914 (M^+), found 822.0910.

Iodine-Induced Transannular Cyclization of 2f under an Inert Atmosphere. To an argon-purged solution of [12]DBA **2f** (34.2 mg, 63.7 μmol) in dry benzene (10 mL) was added iodine (41.0 mg, 162 μmol). The solution was stirred under argon at rt for 90 min. During the reaction, a dark green solid precipitated. The solid was collected by filtration and washed with a small amount of benzene to give *anti*-diiododione **3e** (23.3 mg, 45%). The filtrate was dried to give a brown solid (46.7 mg), whose ^1H NMR spectrum is shown in Figure S1 (Supporting Information). We did not attempt to separate products from the filtrate.

Bromine-Induced Transannular Cyclization of 2f under an Inert Atmosphere: Formation of 5,5,6,11,11,12-Hexabromo-2,3,8,9-tetrabutoxy-5,11-dihydroindeno[1,2-*b*]fluorene (7) and 5,6,12,12-Tetrabromo-2,3,8,9-tetrabutoxyindeno[2,1-*a*]-fluorene-11(12*H*)-one (9). To a solution of [12]DBA **2f** (36.3 mg, 68.2 μmol) in dry CH_2Cl_2 (4 mL) was added bromine (14.0 μL, 273 μmol) in one portion. The mixture was stirred at rt for 15 min. After evaporation of the solvent and excess bromine under reduced pressure, the products were purified by preparative HPLC (eluent: MeCN/CH_2Cl_2 = 7/3) to give **7** (20.6 mg, 30%) as a yellow solid and **9** (30.7 mg, 52%) as an orange solid.

Hexabromide ***7***: mp 178−180 °C dec; ^1H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.16 (s, 2H), 7.37 (s, 2H), 4.19−4.12 (m, 8H), 1.94−1.83 (m, 8H), 1.66−1.47 (m, 8H), 1.03 (t, J = 7.5 Hz, 6H), 1.02 (t, J = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 150.8, 150.1, 147.1, 142.4, 136.0, 125.7, 114.9, 109.7, 108.4, 69.1, 68.8, 51.7, 30.9, 30.8, 19.0, 18.9, 13.58, 13.57; IR (KBr) 2951, 2930, 2871, 1714, 1600, 1508, 1473, 1444, 1427, 1375, 1323, 1246, 1199, 1145, 1063, 996, 892, 863, 848, 790, 757, 734, 580, 558 cm^{-1}. The product was contaminated with a small amount of carbonyl-containing material, which was difficult to remove completely. MS (FD) m/z 1020 (32), 1019 (28), 1018 (78), 1017 (43), 1016 (M^+, base peak), 1015 (32), 1014 (75), 1013 (15) 1012 (32), 874 (23), 873 (14), 872 (39), 871 (10), 870 (25), 858 (23), 857 (12), 856 (36), 855 (11), 854 (22).

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Tetrabromoketone ***9***: mp 160−162 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.02 (s, 1H), 8.01 (s, 1H), 7.38 (s, 1H), 7.29 (s, 1H), 4.20−4.05 (m, 8H), 1.94−1.79 (m, 8H), 1.63−1.47 (m, 8H), 1.07−0.96 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 188.0, 154.2, 151.5, 150.4, 150.2, 146.3, 143.3, 141.8, 138.3, 136.6, 129.8, 127.8, 125.5, 124.1, 122.0, 109.9, 108.64, 108.59, 107.9, 69.3, 69.2, 69.1, 69.0, 45.6, 31.11, 31.07, 31.02, 30.99, 19.22, 19.18, 19.12, 13.8, 13.7; IR (KBr) 2957, 2932, 2872, 1712, 1597, 1578, 1494, 1469, 1447, 1362, 1335, 1280, 1218, 1177, 1147, 1108, 1057, 1026, 996, 967, 929, 870, 854, 759, 750, 730, 563 cm^{-1}; MS (FD) *m*/*z* 876 (22), 875 (27), 874 (70), 873 (38), 872 (M^+, base peak), 871 (26), 870 (67), 868 (18), 731 (13), 730 (32), 728 (63), 727 (12), 726 (30). Anal. Calcd for $C_{36}H_{40}Br_4O_5$: C, 49.57; H, 4.62. Found: C, 49.28; H, 4.29.

Bromine-Induced Transannular Cyclization of 2f under an Oxygen Atmosphere. To a solution of [12]DBA **2f** (40.4 mg, 75.3 μmol) in oxygen-bubbled dry CH_2Cl_2 (4 mL) was added bromine (16.0 μL, 312 μmol) dropwise. The solution was stirred vigorously under oxygen at rt for 40 min. Evaporation of the solvent and excess bromine under reduced pressure a gave brown solid (67.1 mg), whose ^{1}H NMR spectrum is shown in Figure S4 (Supporting Information). We did not attempt to separate products from this material.

Hydrolysis of 7: 5,11-Dibromo-2,3,8,9-tetrabutoxyindeno-[1,2-*b*]fluorene-6,12-dione (3g). To a suspension of hexabromide **7** (12.0 mg, 11.8 μmol) and NaOAc (49.0 mg, 598 μmol) in CH_2Cl_2 (5 mL) was added 50% aqueous AcOH (5 mL). The mixture was stirred at rt for 13 h and then diluted with CH_2Cl_2 and a saturated aqueous solution of $NaHCO_3$. The aqueous layer was separated and extracted with CH_2Cl_2. The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ and brine and then dried over $MgSO_4$. After removal of the solvent under reduced pressure, the product was purified by silica gel column chromatography ($CHCl_3$ only) to give the diketone **3g** (7.9 mg, 92%) as a dark green solid: mp 239−240 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 8.10 (s, 2H), 7.19 (s, 2H), 4.17 (t, *J* = 6.5 Hz, 4H), 4.07 (t, *J* = 6.5 Hz, 4H), 1.92−1.78 (m, 8H), 1.65−1.46 (m, 8H), 1.01 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 188.8, 154.5, 150.2, 145.8, 137.3, 136.1, 127.0, 112.9, 109.0, 108.9, 69.25, 69.16, 31.09, 31.05, 19.23, 19.18, 13.9, 13.8; IR (KBr) 2957, 2934, 2911, 2871, 1708, 1583, 1505, 1465, 1448, 1427, 1376, 1323, 1297, 1280, 1246, 1213, 1118, 1061, 1023, 963, 868, 808, 780, 735, 676, 656, 555 cm^{-1}; HRMS (FAB) calcd for $C_{36}H_{40}O_6{}^{79}Br_1{}^{81}Br_1$ 728.1171 (M^+), found 728.1190.

Hydrolysis of 9: 5,6-Dibromo-2,3,8,9-tetrabutoxyindeno-[2,1-*a*]fluorene-11,12-dione (6b). To a suspension of tetrabromide **9** (10.1 mg, 11.6 μmol) and NaOAc (38.0 mg, 463 μmol) in 50% aqueous AcOH (5 mL) was added CH_2Cl_2 (5 mL). The mixture was stirred at rt for 13 h and then diluted with CH_2Cl_2 and a saturated aqueous solution of $NaHCO_3$. The aqueous layer was separated and extracted with CH_2Cl_2. The combined organic layers were washed with a saturated aqueous solution of $NaHCO_3$ and brine and then dried over $MgSO_4$. Removal of the solvent under reduced pressure gave the diketone **6b** (7.1 mg, 85%) as an orange solid: mp 226−228 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 30 °C) δ 7.99 (s, 2H), 7.23 (s, 2H), 4.15 (t, *J* = 6.5 Hz, 4H), 4.07 (t, *J* = 6.5 Hz, 4H), 1.94−1.80 (m, 8H), 1.63−1.48 (m, 8H), 1.07−0.99 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, 30 °C) δ 187.6, 154.1, 150.6, 142.8, 137.9, 133.5, 128.0, 124.3, 108.4, 108.3, 69.2, 69.0, 31.1, 19.24, 19.18, 13.87, 13.84; IR (KBr) 2956, 2925, 2854, 1743, 1720, 1576, 1494, 1466, 1360, 1335, 1281, 1214, 1112, 1071, 1047, 968, 906, 869, 794, 768, 725, 640 cm^{-1}; HRMS (FAB) calcd for $C_{36}H_{40}O_6{}^{79}Br_1{}^{81}Br_1Na_1$ 751.1069 [$(M + Na)^+$], found 751.1078.

Computational Methods. DFT calculations were performed with the Gaussian 03 program package.[13] The geometries were optimized using the B3LYP method with the 6-31G* (for C, H, and O) and LANL2DZ (for Br and I) basis sets. The natures of the stationary points were assessed by means of vibration frequency analysis.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR spectrum of the dried filtrate in the reaction of **2f** with iodine under an inert atmosphere. ^{1}H NMR spectra of the crude product of the reaction of **2f** with bromine or iodine under an oxygen atmosphere. ^{1}H and ^{13}C NMR spectra of the crude product of the reaction of **2f** with bromine under an inert atmosphere and selected new compounds **3e**,**g**, **6a**,**b**, and **7**. ORTEP drawing and CIF file of **7**. Frontier molecular orbitals and Mulliken charge distributions (at C7 and C8) of intermediates **5X** (R = OMe, X = Br and I, and R = H, X = Br and I). Cartesian coordinates for the optimized geometries of **1X**, **4X**, and **5X** (R = OMe, X = Br and I, and R = H, X = Br and I). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) DFT calculations at the B3LYP/ 6-31G* and LANL2DZ level of theory showed that the HOMO energy level of methoxy-substituted **1X** (R = OMe, X = I) is 0.43 eV higher than that of the parent **1X** (R = H, X = I).
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