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Preparation and Molecular Structures of 9,10-Dihydrophenanthrenes: Substituent Effects on the Long Bond Length

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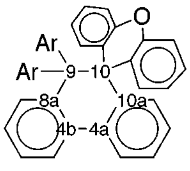
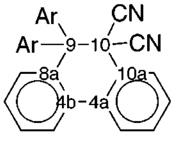
9,10-Dihydrophenanthrene derivatives **1**−**3** with electron-donating and/or -accepting groups at their 9,10-positions were prepared, and their precise molecular structures were determined by X-ray analyses at 203 K. The long C^9-C^{10} bond [1.646(4) Å] in the hexaarylethane-type compound **1** with four electron-donating groups is mainly caused by steric interaction. Push−pull type substitution does not induce the elongation of the central bond in the present system; the corresponding distance in 9,9-bis(4-dimethylaminophenyl)-10,10-dicyano derivative **2** [1.599(4) Å] is intermediate between those of **1** and the tetracyano compound **3** [1.587(2) Å].

Covalent bond lengths such as 1.54 Å for $C_{sp^3}-C_{sp^3}$ are basic parameters in chemistry.[1] Examples that show remarkable deviation from standard values have attracted chemists' attention, and novel concepts that have been proposed based on these differences, such as $\pi-\sigma-\pi$ through-bond (TB) interaction,[2] can be generalized for a better understanding of fundamental chemistry.[3] In this regard, the bond lengths greater than 1.72 Å found in 1,1,2,2-tetraphenylbenzocyclobutene derivatives by Toda et al.[4] are noteworthy, since they have been shown to be not merely artifacts during crystallographic analyses.[5,6] Theoretical calculations also support the intrinsic nature of their lengths,[7,8] although the origin of this elongation is still unclear.[5,8]

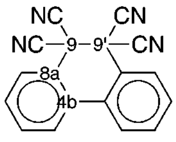
In the course of our study of molecular systems whose structures and properties can be controlled electrochemically, we have found that the central bond in the electron-donating hexaphenylethane (HPE) derivative **1** is quite long [1.643(6) Å at 296 K]. This expansion may be responsible for its facile mesolytic fission upon one-electron oxidation.[9] Considering the proposal that pre-strained bonds are more susceptible to perturbation with regard to bond length,[8,10] it would be interesting to further explore 9,10-dihydrophenanthrene-type compounds. The main purpose of this study was to address the question of whether push−pull type substitution[11] as in **N** in Scheme 1 plays a role in elongation of the C^9-C^{10} bond by enhanced ($\pi-\sigma^*$)-type TB interaction along with the contribution of a bond-dissociated zwitterionic structure[12] like **Z**.



1



2



3

(Ar = *p*-$Me_2NC_6H_4$)

We conducted detailed comparisons of the precise molecular geometries of 9,10-dihydrophenanthrenes **1**−**3** determined by X-ray analyses at 203 K, where the latter two compounds were newly designed for this purpose. With regard to the negation of steric factors, the ideal system for comparisons might be a series of 9,9,10,10-tetraaryl derivatives,[13] in which only the aryl substituents at *para*-positions differ electronically. However, with such “globular” ethanes, it is often difficult to determine the correct bond lengths due to structural disorder in the crystal.[13,14a] Accordingly, we decided to attach electron-withdrawing cyano groups directly to the 9 and/or 10

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[11] While push−pull type substitution has been predicted to elongate or even break the C^1-C^4 bond in 1,4-disubstituted bicyclo-[2.2.0]hexane by the MNDO method (ref 10), this idea has recently been challenged by ab initio techniques (RHF/6-31G(d)): Baldridge, K. K.; Battersby, T. R.; Clark, R. V.; Siegel, J. S. *J. Am. Chem. Soc.* **1997**, *119,* 7048.

[12] Formation of a ring-closure zwitterionic structure was recently studied in *N,N*-dimethyl-1-naphthylamine derivatives with an electron-deficient alkenyl moiety at the 8 position: Bell, P. C.; Wallis, J. D. *Chem. Commun.* **1999**, 257.

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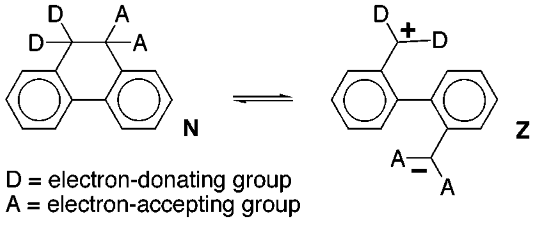
Scheme 1



positions in **2** and **3**, so our discussion also addresses steric factors between the substituents.

Results and Discussion

Preparation. Dihydrophenanthrene derivatives **1**−**3** were prepared according to Scheme 2. The reaction of a mixture of Michler's ketone and xanthone with 2,2′-dilithiobiphenyl derived from diiodide **4** gave the unsymmetric diol **5** (yield 9%) after chromatographic separation from two symmetric diols. Treatment with HBF_4 gave the strongly colored dication $\mathbf{6}^{2+}$, which was isolated in 93% yield as a stable salt. Reductive cyclization by SmI_2 proceeded smoothly to give colorless HPE derivative **1** in 78% yield.

When 2,2′-diiodobiphenyl **4** was subjected to Takahashi's arylenebis(malononitrile) preparation,[15] tricyclic enaminonitrile **11** was obtained in 56% yield, which may be formed by isomerization of the primary product **10** through Thorpe-type condensation.[16] Oxidative treatment of **11** with NCS gave the desired tetracyano derivative **3** (yield 35%) along with bis(chlorodicyanomethyl)biphenyl **12** (yield 42%), which could be converted to **3** in 70% yield by treatment with Zn dust.

2-Formyl-2′-iodobiphenyl **7** was obtained in 16% yield through a one-pot reaction from biphenyl, and its condensation with dimethylaniline gave the triarylmethane derivative **8** in 54% yield. Pd-catalyzed substitution gave the dicyanomethylated product **9** in 73% yield, from which the push−pull compound **2** was obtained quantitatively by dehydrogenation with Ag_2O.

Spectral Properties. Electronic spectra of **1**−**3** measured in MeCN clearly show that all of the compounds exhibit absorption only in the UV region (Figure 1). Although a zwitterionic form such as **Z** in Scheme 1 might be stabilized in such a polar solvent, the characteristic absorption band of the $(p\text{-}Me_2NC_6H_4)_2CPh^+$ chromophore [λ_{max} (MeCN) 619 nm (log ϵ 5.07)] is absent in the spectrum of the push−pull type compound **2**. The zwitterionic form of **2** could not be detected even under photolytic conditions (100 W Hg lamp, quartz),[17] suggesting that the equilibrium in Scheme 1 lies far to the left in the case of **2**.

This idea is also supported by comparing the ^{13}C NMR chemical shifts for C^9 and C^{10}. The values for *C*(CN)$_2$ are 49.63 and 45.77 ppm for **2** and **3**, respectively, whereas those for *C*Ar$_2$ are 59.58 and 62.82 ppm for **2** and 9,9,10,10-tetrakis(4-dimethylaminophenyl)-9,10-dihydrophenanthrene.[13] The similarity of the values for each pair indicates negligible polarization of the C^9−C^{10} bond in **2**.

Table 1. Geometric Parameters for 1−3 Determined by X-ray Analyses at 203 K[a]

	1	**2**	**3**[b]
X	*p*-$Me_2NC_6H_4$	*p*-$Me_2NC_6H_4$	CN
Y	spiro-9,9′-xanthene	CN	CN
d_1 (C^9−C^{10})/Å	1.646(4)	1.599(4)	1.587(2)
d_2 (C^{8a}−C^9)/Å	1.538(4)	1.531(5)	1.528(2)
$d_{2'}$ (C^{10}−C^{10a})/Å	1.528(4)	1.532(5)	−
d_3 (C^9−$C^{X(ax)}$)/Å	1.551(4)	1.546(4)	1.489(2)
$d_{3'}$ (C^9−$C^{X(eq)}$)/Å	1.549(4)	1.532(5)	1.476(2)
d_4 (C^{10}−$C^{Y(ax)}$)/Å	1.546(4)	1.488(5)	−
$d_{4'}$ (C^{10}−$C^{Y(eq)}$)/Å	1.544(4)	1.473(6)	−
ϕ (C^{8a}−C^9−C^{10}−C^{10a})/°	40.4(3)	63.2(3)	63.2(2)

[a] $C^{(ax)}$ and $C^{(eq)}$ denote the carbon atoms of the substituents at pseudoaxial and pseudoequatorial positions in the half-chair conformation, respectively. [b] Molecule on the crystallographic C_2 axis [$C^{10} = C^{9'}$; $C^Y(ax) = C^X(ax)'$; $C^Y(eq) = C^X(eq)'$].

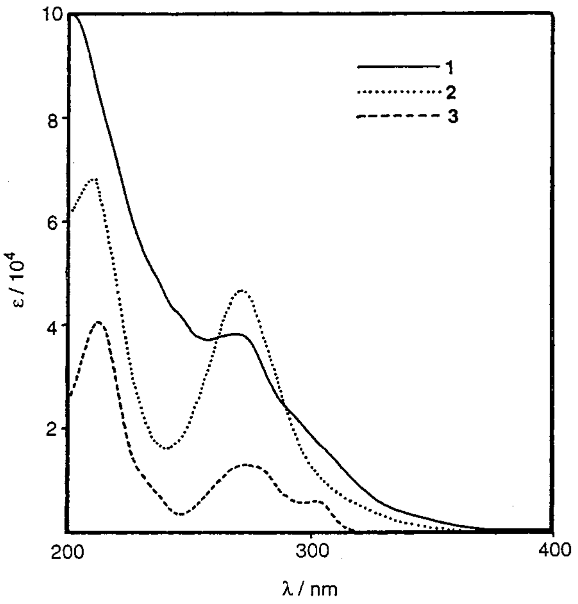


Figure 1. Electronic spectra of **1**−**3** measured in MeCN.

Molecular Structures Determined by X-ray Analyses. X-ray structural analyses were carried out on carefully grown single crystals of **1**−**3** using a CCD camera apparatus at 203 K. Selected geometrical data shown in Table 1 were determined on the basis of these measurements. Reflection data collected under other conditions (at 296 K and/or using a four-circle diffractometer) were also used for comparisons to confirm the absence of any systematic errors in the analyses. The central six-membered rings in **1**−**3** adopt the pseudo half-chair conformation. No structural disorder was observed in any case. The thermal ellipsoids for C^9 and C^{10} in **1**−**3** are small with an approximately round shape (Figure S1 in Supporting Information).

The central C^9−C^{10} bond (d_1) in quadruply aryl-substituted compound **1** is fairly long [1.646(4) Å]. Such elongation may be accounted for by the severe steric repulsion inherent in the HPE-type skeleton,[14] or might result from TB interaction between the aryl substituents located on C^9 and C^{10}. When the latter interaction is more important, the flanking bonds are expected to be shortened.[6a] However, all of these bonds are longer than the standard (1.51 Å for C_{sp^3}−C_{Ar}).[1] The smallest value [$d_{2'}$: 1.528(4) Å] is found for that connected to the

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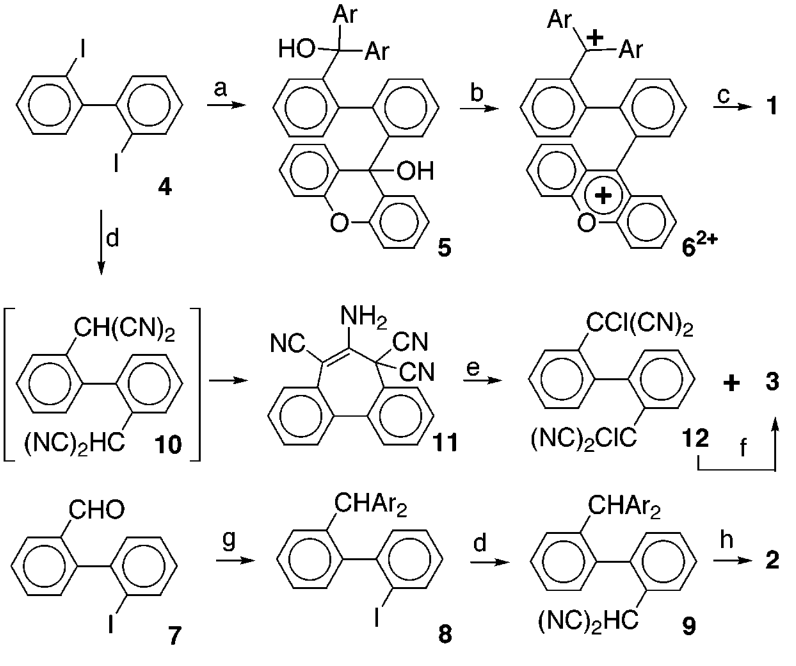
(17) This result is in sharp contrast to the photodissociative chromic behavior of the colorless adduct of malachite green with dicyanomethylide [Ar_2PhC−$CH(CN)_2$] with the same chromophore as **2**: Suzuki, T.; Ono, K.; Tsuji, T, unpublished data.

Scheme 2



(Ar = *p*-$Me_2NC_6H_4$)

a) i *n*-BuLi, ii $Ar_2C{=}O$ and xanthone; b) $HBF_4/(EtCO)_2O$; c) SmI_2; d) $NaCH(CN)_2$, Pd cat; e) NCS, Et_3N; f) Zn; g) ArH, $ZnCl_2$; h) Ag_2O.

biphenyl skeleton. By considering the direction of the p-lobes at C^{8a} and C^{10a}, however, $\pi{-}\sigma{-}\pi$ TB interaction through the array $C^{8a}{-}C^9{-}C^{10}{-}C^{10a}$ is unlikely,[18] indicating that the expansion of the central bond is mainly caused by steric factors that also elongate the flanking bonds.

It is of special interest that d_1 in the push−pull compound **2** [1.599(4) Å] is smaller than that of **1**, although it is still larger than the standard. Again, all of the flanking bonds in **2** are longer than the standard (1.47 Å for $C_{sp^3}{-}C_{cyano}$).[1] Even though the difference between the $C^9{-}C^{X(ax)}$ [d_3: 1.546(4) Å] and $C^9{-}C^{X(eq)}$ [$d_{3'}$: 1.532(5) Å] lengths may suggest TB interaction of the π-orbital at $C^{X(eq)}$, the direction of its lobe is not suitable for overlap with the $C^9{-}C^{10}$ σ bond.[19] On the other hand, all of the flanking bonds in **1**−**3** to axial substituents (d_3 and d_4) are longer than those to equatorial ones ($d_{3'}$ and $d_{4'}$),[20] indicating that this could be explained by repulsive interaction between the axial substituents and the p-lobes at C^{8a} or C^{10a}.

Conclusion

The $C^9{-}C^{10}$ bond in **3**, which has less bulky cyano groups, is the shortest [1.587(2) Å] among the compounds examined here, and the observed tendency with regard to d_1 (**1** > **2** > **3**) can be explained by the different degrees of steric hindrance caused by the bulky aryl substituents. The torsion angle of $C^{8a}{-}C^9{-}C^{10}{-}C^{10a}$ which describes the twisting of the half-chair conformation seems correlated to d_1 by changing the degree of "front strain" between the substituents.[14c] Compounds **2** and **3** seem to reduce such repulsion by adopting a torsion angle of 63.2° (gauche-type), whereas that value in **1** is only 40.4(3)° probably due to the torsional strain induced by the rigid spiro-type connection of a xanthene unit. Since the front strain may also be reduced by expansion of the central bond, steric factors seem to be most responsible for the long $C^9{-}C^{10}$ bond in **1**. Compounds with a smaller torsion angle like **1** are also expected to have a long $C_{sp^3}{-}C_{sp^3}$ bond.[21] In this study, we did not find any convincing evidence that $\pi{-}\sigma{-}\pi$ TB interaction[22] causes elongation of the prestrained $C^9{-}C^{10}$ bond in the dihydrophenanthrene skeleton, even when a push−pull type substitution is applied.

Experimental Section

Preparation of Spiro[10,10-bis(4-dimethylaminophenyl)-9,10-dihydrophenanthrene-9,9′-[9H]xanthene] 1. To a colorless solution of 2,2′-diiodobiphenyl **4**[23] (2.04 g, 5.02

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[18] Parallelism between the p-lobes and the $C^9{-}C^{10}$ bond is necessary to realize TB interaction, yet the torsion angles for $C^{ortho}{-}C^{8a}{-}C^9{-}C^{10}$ [−29.2(3)° and 158.7(3)°] and for $C^{ortho}{-}C10^a{-}C^{10}{-}C^9$ [−27.7(4)° and 157.0(3)°] are far from the ideal value (±90.0°). The corresponding values involving C^X and C^Y are much closer to ±90.0°: $C^{ortho}{-}C^{X(ax)}{-}C^9{-}C,^{10}$ −143.1(3)° and 47.3(4)°; $C^{ortho}{-}C^{X(eq)}{-}C^9{-}C,^{10}$ −91.7(3)° and 80.6(3)°; $C^{ortho}{-}C^{Y(ax)}{-}C^{10}{-}C,^9$ −98.2(3)° and 78.6(3)°; $C^{ortho}{-}C^{Y(eq)}{-}C^{10}{-}C,^9$ −81.4(3)° and 97.3(3)°.

[19] The torsion angles describing the direction of p-lobes of Ar groups in **2** are as follows: $C^{ortho}{-}C^{X(ax)}{-}C^9{-}C,^{10}$ −51.2(4)° and 131.5(3)°; $C^{ortho}{-}C^{X(eq)}{-}C^9{-}C,^{10}$ −63.1(4)° and 115.5(4)°.

[20] Considering the "trans rule" in TB interaction, the π orbitals of $C^{X(ax)}$ and $C^{Y(ax)}$ should be much more involved than those of $C^{X(eq)}$ and $C^{Y(eq)}$ because of the antiperiplanar arrangement of the $C^{X(ax)}{-}C^9{-}C^{10}{-}C^{Y(ax)}$ bond array [torsion angle: 166.4(2)° in **1**; 169.1(3)° in **2**; 174.2(1)° in **3**]. Thus, the observed tendency ($d_3 > d_{3'}$; $d_4 > d_{4'}$) is inconsistent with the assumption that TB interaction via $C^9{-}C^{10}$ affects the bond lengths. Review on the "trans rule": Paddon-Row: M. N. *Acc. Chem. Res.* **1982**, *15*, 245.

[21] Based on the X-ray analysis (203 K) of 1,1-bis(4-dimethylaminophenyl)-2,2-dicyanoindan which has the same substructure as **2**, the bond length for $C^1{-}C^2$ [1.627(4) Å] is much longer than $C^9{-}C^{10}$ in **2**, which may be related to the smaller torsion angle of 19.3(2)° for $C^{7a}{-}C^1{-}C^2{-}C^3$: Suzuki, T.; Ono, K.; Tsuji, T, unpublished data.

[22] A new explanation for bond elongation other than TB interaction was recently given: Ósawa, S.; Sakai, M.; Ósawa, E. *J. Phys. Chem. A* **1997**, *101*, 1378.

mmol) in dry THF (20 mL) was added dropwise *n*-BuLi (1.47 mol dm^{-3} in *n*-hexane, 7.10 mL, 10.4 mmol) at 0 °C under Ar, and the mixture was stirred for 10 min at this temperature. To the resultant suspension of 2,2′-dilithiobiphenyl was added a mixture of 4,4′-bis(dimethylamino)benzophenone (1.30 g, 4.85 mmol) and xanthone (971 mg, 4.95 mmol) in dry THF (90 mL). After stirring for 2 h at room temperature, the reaction was quenched by adding water. THF was evaporated, and the residue was extracted with benzene. The organic layer was washed with water and brine and dried over Na_2SO_4. Evaporation of the solvent gave 3.66 g of oily material containing 9-[2′-bis(4-dimethylaminophenyl)hydroxymethylbiphenyl-2-yl]-9-hydroxyxanthene **5**. Two symmetric diols, biphenyl-2,2′-diylbis(9-hydroxyxanthene) **5′** and 2,2′-bis[bis(4-dimethylaminophenyl)hydroxymethyl]biphenyl **5″**,[24] were also formed in this reaction. Chromatographic separation on SiO_2 (AcOEt/*n*-hexane, 1/4−1/2) followed by recrystallization from MeOH gave **5** as colorless crystals (250 mg, yield 8.6%). An authentic sample of **5′** was prepared by the similar reaction of 2,2′-dilithiobiphenyl with 2 equiv of xanthone (62% yield).

To a solution of unsymmetric diol **5** (70 mg, 0.11 mmol) in DME (3 mL) was added propionic anhydride (0.5 mL) followed by 42% HBF_4 (50 μL, 0.34 mmol), and the mixture was heated at 80 °C for 1 h. By slow cooling to room temperature, dication salt $\mathbf{6}^{2+}(BF_4^-)_2$ separated as a deep-green solid (80 mg, yield 93%), which was filtered, washed with DME, and dried in vacuo.

To a suspension of $\mathbf{6}^{2+}(BF_4^-)_2$ (30 mg, 0.040 mmol) in dry THF (10 mL) was added SmI_2 (0.1 mol dm^{-3} in THF, 1.7 mL, 0.17 mmol) at room temperature. The deeply colored suspension gradually turned colorless during the addition. After stirring for 30 min and evaporation of THF, the residue was suspended in water and extracted with CH_2Cl_2. The organic layer was washed with water and brine and dried over Na_2SO_4. Evaporation of solvent followed by separation by preparative TLC (SiO_2, AcOEt/*n*−hexane, 1/4) gave HPE derivative **1** as colorless crystals (18 mg, yield 78%).

Data of **5**: mp 143−152 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) δ/ppm 7.63 (1H, dd, $J = 7.8$, 1.5 Hz), 7.39 (1H, dd, $J = 7.8$, 1.5 Hz), 7.32 (1H, ddd, $J = 7.8$, 7.8, 1.5 Hz), 7.10−7.24 (6H, m), 7.02 (AA′XX′, 2H), 6.95−7.00 (2H, m), 6.86 (AA′XX′, 2H), 6.83−6.92 (3H, m), 6.72 (1H, ddd, $J = 7.8$, 7.8, 1.5 Hz), 6.64 (AA′XX′, 2H), 6.59 (AA′XX′, 2H), 6.18 (1H, dd, $J = 7.8$, 1.5 Hz), 5.72 (1H, s), 3.02 (1H, s), 2.94 (6H, s), 2.93 (6H, s); IR (KBr) 3432, 1612, 1520, 1478, 1450, 758 cm^{-1}; FD-MS *m*/*z* 618 (M^+, BP). Anal. Calcd for $C_{42}H_{38}N_2O_3$: C, 81.53; H, 6.19; N, 4.53. Found: C, 81.60; H, 6.19; N, 4.40. Data of **5′**: colorless solid, mp 128−133 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) δ/ppm 7.64 (2H, dd, $J = 8.0$, 1.5 Hz), 7.34 (2H, ddd, $J = 8.0$, 8.0, 1.5 Hz), 7.22−7.30 (6H, m), 7.04−7.20 (10H, m), 6.98 (2H, ddd, $J = 8.0$, 8.0, 1.5 Hz), 6.82 (2H, dd, $J = 8.0$, 1.5 Hz); IR (KBr) 3420, 1478, 1450, 1240, 756 cm^{-1}; EI-MS *m*/*z* (relative intensity) 528 ($M^+ - H_2O$, 100), 512 (21), 331 (84). Anal. Calcd for $C_{38}H_{26}O_4$: C, 83.50; H, 4.79. Found: C, 83.39; H, 4.86. Data of $\mathbf{6}^{2+}(BF_4^-)_2$: mp 219−220 °C (dec); ^{1}H NMR (400 MHz, CD_3CN, 50 °C) δ/ppm 8.40 (2H, br), 8.23 (2H, br d, $J = 8.5$ Hz), 7.90 (2H, br d, $J = 8.5$ Hz), 7.78−7.84 (3H, br m), 7.46−7.56 (3H, br m), 7.32 (2H, ddd, $J = 7.8$, 7.8, 1.0 Hz), 7.26−7.30 (1H, br m), 6.85 (2H, br d, $J = 7.8$ Hz), 6.20−7.20 (7H, br), 3.30 (6H, br s), 3.29 (6H, br s); IR (KBr) 1620, 1584, 1374, 1174, 1084, 1036 cm^{-1}; FAB-MS *m*/*z* (relative intensity) 584 (M^+, 100), 671 ($M^+ + BF_4$, 8). Anal. Calcd for $C_{42}H_{36}N_2OB_2F_8$: C, 66.52; H, 4.78; N, 3.69. Found: C, 66.64; H, 4.79; N, 3.76. Data of **1**: mp 294−295 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) δ/ppm 8.03 (1H, d, $J = 7.5$ Hz), 7.90 (1H, d, $J = 7.5$ Hz), 7.46 (1H, ddd, $J = 7.5$, 7.5, 1.5 Hz), 7.34 (1H, dd, $J = 7.8$, 1.5 Hz), 7.22−7.30 (3H, m), 7.13−7.19 (2H, m), 6.88−7.04 (3H, m), 6.63−6.72 (6H, m), 6.61 (2H, dd, $J = 8.3$, 1.5 Hz), 6.24 (4H, AA′XX′), 2.84 (12H, s); IR (KBr) 1610, 1518, 1480, 1440, 1312, 750 cm^{-1}; FD-MS *m*/*z* 584 (M^+, BP); UV (MeCN) λ_{max} 270 (log ϵ 4.58), 200 sh (5.00). Anal. Calcd for $C_{42}H_{36}N_2O$: C, 86.27; H, 6.21; N, 4.79. Found: C, 86.04; H, 6.41; N, 4.65.

Preparation of 9,9-Bis(4-dimethylaminophenyl)-10,10-dicyano-9,10-dihydrophenanthrene 2. Crystalline 2,2′-dilithiobiphenyl·$TMEDA_2$ complex[23] was prepared from biphenyl (4.30 g, 24.0 mmol) and *n*-BuLi (1.43 mol dm^{-3} in *n*-hexane, 46.0 mL, 65.8 mmol) in TMEDA (10 mL). Without filtration of the moisture-sensitive complex, supernatant was removed using a syringe. To a THF (10 mL) solution of this solid (6.20 g) was added dropwise a mixture of 1,2-diiodoethane (6.59 g, 23.4 mmol) and DMF (4.41 g, 70.1 mmol) in dry THF (10 mL) at −78 °C over 15 min. The temperature of the cooling bath was gradually (overnight) raised to room temperature. After addition of 10% $Na_2S_2O_3$ aq and evaporation of THF, the residue was extracted with $CHCl_3$. From the extract was obtained 6.98 g of reddish oil, which was chromatographed on SiO_2 (*n*-hexane; *n*-hexane/benzene 1/4−1/1; $CHCl_3$). The first eluate gave 1.59 g of 2,2′-diiodobiphenyl **4** (yield 25%), and the second eluate gave 2-formyl-2′-iodobiphenyl as colorless rods **7** (772 mg, yield 16% based on biphenyl). Further eluates contained 2,2′-diformylbiphenyl **7′** and other polar byproducts. When the similar reaction of 2,2′-dilithiobiphenyl was conducted using an equimolar mixture of 1,2-diiodoethane and DMF, the product ratio of **4**:**7**:**7′** determined by gas chromatography was 20:11:2.

A mixture of **7** (200 mg, 0.649 mmol), *N*,*N*-dimethylaniline (196 mg, 1.62 mmol), $ZnCl_2$ (74 mg, 0.54 mmol), and urea (33 mg, 0.54 mmol) was heated at 95 °C for 4.5 h with vigorous stirring. After being cooled, the mixture was triturated with benzene and insoluble material was removed by filtration. Chromatographic separation on SiO_2 (*n*-hexane/$CHCl_3$ 1/1) gave 2-[bis(4-dimethylaminophenyl)methyl]-2′-iodobiphenyl **8** (185 mg, yield 54%) as colorless crystals.

Mineral oil of NaH (104 mg, 60%, 1.73 mmol) was removed by washing with *n*-hexane. To its suspension in dry THF (20 mL) was added malononitrile (57 mg, 0.86 mmol) at 0 °C. After gas evolution ceased, iodide **8** (90 mg, 0.17 mmol) and $(Ph_3P)_2PdCl_2$ (24 mg, 0.034 mmol) were added to the flask. The mixture was heated at reflux for 72 h under Ar. After evaporation of THF, the residue was suspended in water and its pH was adjusted to 10 with dil NaOH, and it was extracted with AcOEt. The combined organic layers were washed with brine and dried over Na_2SO_4. Evaporation of solvent followed by separation by gel-permeation recycling preparative HPLC ($CHCl_3$, JAIGEL H1-H2 on LC-908) gave unreacted **8** (34 mg, 38% recovery) and 2-[bis(4-dimethylaminophenyl)methyl]-2′-dicyanomethylbiphenyl **9** as a colorless solid (36 mg, yield 46%; yield 73% based on consumption).

To a solution of dihydro derivative **9** (15 mg, 0.032 mmol) in benzene (1 mL) were added Ag_2O (30 mg, 0.13 mmol) and $MgSO_4$ (30 mg), and the mixture was stirred at room temperature for 40 h. Insoluble material was removed by suction, and separation by preparative TLC (SiO_2, CH_2Cl_2) gave **2** as a colorless solid (16 mg, yield 100%).

Data of **7**: mp 90−90.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) δ/ppm 9.77 (1H, d, $J = 1.0$ Hz), 8.04 (1H, dd, $J = 7.5$, 1.5 Hz), 7.97 (1H, dd, $J = 7.5$, 1.5 Hz), 7.67 (1H, ddd, $J = 7.5$, 7.5, 1.5 Hz), 7.56 (1H, br dd, $J = 7.5$, 7.5 Hz), 7.44 (1H, ddd, $J = 7.5$, 7.5, 1.5 Hz), 7.32 (1H, dd, $J = 7.5$, 1.5 Hz), 7.28 (1H, br d, $J = 7.5$ Hz), 7.13 (1H, ddd, $J = 7.5$, 7.5, 1.5 Hz); IR (KBr) 2856, 2760, 1690, 1594, 770, 758, cm^{-1}; EI-MS *m*/*z* (relative intensity) 308 (M^+, 100%), 181 (95). Anal. Calcd for $C_{13}H_9OI$: C, 50.67; H, 2.94. Found: C, 50.77; H, 3.04. Data of **8**: mp 129−131 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) δ/ppm 7.92 (1H, dd, $J = 7.5$, 1.5 Hz), 7.32 (1H, ddd, $J = 7.5$, 7.5, 1.5 Hz), 7.25 (1H, ddd, $J = 7.5$, 7.5, 1.5 Hz), 7.12 (1H, br d, $J = 7.5$ Hz), 7.11 (1H, br dd, $J = 7.5$, 7.5 Hz), 7.05 (1H, dd, $J = 7.5$, 1.5 Hz), 7.01−6.94 (3H, m), 6.72−6.53 (7H, br m), 5.03 (1H, s), 2.90 (6H, s), 2.89 (6H, s); IR (KBr) 1614, 1518, 1346, 754 cm^{-1}; EI-MS *m*/*z* (relative intensity) 532 (M^+, 100%), 405 (86), 284 (50), 253 (44). Anal. Calcd for $C_{29}H_{29}N_2I$: C, 65.41; H, 5.49; N, 5.26. Found: C, 65.93; H, 5.57 N, 5.23; HRMS calcd 532.1378, observed 532.1377. Data of **9**: mp 167−168.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) δ/ppm 7.62 (1H, m), 7.56−7.48 (2H, m), 7.37 (1H, ddd, $J = 7.5$, 7.5, 1.5 Hz), 7.35 (1H,

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m), 7.29 (1H, br dd, $J = 7.5, 7.5$ Hz), 7.22−7.18 (2H, m), 6.84 (2H, AA′XX′), 6.69−6.57 (6H, m), 5.05 (1H, s), 3.87 (1H, s), 2.91 (12H, s); IR (KBr) 1612, 1520, 1353, 764 cm^{-1}; FD-MS m/z 470 (M^+, BP). Anal. Calcd for $C_{32}H_{30}N_4$·$0.5H_2O$: C, 80.14; H, 6.51; N, 11.68. Found: C:80.54, H:6.54, N:11.48. Data of **2**: mp 260.5−261.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 24 °C) δ/ppm 8.1−7.9 (1H, br), 7.82 (1H, br d, $J = 7.5$ Hz), 7.77 (1H, dd, $J = 7.5, 1.0$ Hz), 7.71 (1H, br d, $J = 7.5$ Hz), 7.47−7.33 (5H, m), 7.0−6.9 (2H, br), 6.9−6.5 (3H, br), 6.4−6.3 (2H, br), 2.99 (6H, br s), 2.81 (6H, br s); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C) δ/ppm 40.16, 40.18, 49.63, 59.58, 111.26, 111.30, 125.18, 125.47, 126.02, 128.11, 128.43, 128.59, 128.63, 128.67, 128.69, 128.92, 129.47, 130.1 (br), 131.92, 131.95, 132.05, 132.18, 132.34, 133.01, 133.24, 138.93; IR (KBr) 1610, 1522, 1452, 1362, 1216, 1166, 810 cm^{-1}; UV (MeCN) λ_{max} 271 (log ϵ 4.67), 209 (4.84); FD-MS m/z 468 (M^+, BP); HRMS calcd 468.2316, observed 468.2323. When **2** was recrystallized from ether, one molecule of solvent was incorporated as crystallization solvent. Anal. Calcd for $C_{32}H_{28}N_4$·$C_4H_{10}O$: C, 79.67; H, 7.06; N, 10.32. Found: C, 80.15, H, 6.82, N, 10.25.

Preparation of 9,9,10,10-Tetracyano-9,10-dihydrophenanthrene 3. To a suspension of NaH (850 mg, 60% in oil, 21.2 mmol) in dry THF (10 mL) was added malononitrile (932 mg, 14.1 mmol). After gas evolution ceased, 2,2′-diiodobiphenyl **4** (1.41 g, 3.47 mmol) and $(Ph_3P)_4Pd$ (435 mg, 0.376 mmol) were added to the flask. The mixture was heated at reflux for 63 h under Ar. After adding water, the basic aqueous layer was washed with CH_2Cl_2. After acidifying with dil HCl to pH 2 and extraction with CH_2Cl_2, the combined extracts were washed with brine and dried over Na_2SO_4. Evaporation of the solvent followed by recrystallization from EtOH gave 6-amino-5,7,7-tricyanodibenzo[*ac*]cycloheptatriene **11** as colorless rods (548 mg, 56%).

Enaminonitrile **11** (343 mg, 1.22 mmol) was ground in a mortar into a fine powder. To its suspension in THF (20 mL) was added NCS (334 mg, 2.50 mmol) followed by Et_3N (0.2 mL). After stirring at room temperature for 20 h, the solvent was evaporated and the residue was chromatographed on SiO_2 (AcOEt/*n*-hexane, 1/4). The first eluate gave colorless crystals of 2,2′-bis(chlorodicyanomethyl)biphenyl **12** (142 mg, yield 42%) upon recrystallization from EtOH. Compound **3** (123 mg, yield 35%) was obtained as colorless rods from the second eluate after recrystallization from EtOH.

To a solution of **12** (72 mg, 0.20 mmol) in MeCN (5 mL) was added Zn dust (128 mg, 1.96 mmol), and the mixture was stirred for 48 h at room temperature. After being diluted with $CHCl_3$ (20 mL) and removal of insoluble material, the colorless solution was concentrated and separated by preparative TLC (SiO_2, $CHCl_3$) to give 39 mg of **3** as a colorless solid in 70% yield.

Data of **11**: mp 225−227 °C; ^{1}H NMR (90 MHz, $CDCl_3$, 24 °C) δ/ppm 7.90−7.40 (8H, m), 5.30 (2H, br s); IR (KBr) 3428, 3336, 2200, 1638, 1592, 750 cm^{-1}; EI-MS m/z (relative intensity) 282 (M^+, 88), 218 (100). Anal. Calcd for $C_{18}H_{10}N_4$: C, 76.58; H, 3.57; N, 19.85. Found: C, 76.69; H, 3.70, N: 19.66. Data of **12**: mp 183.5−184.5 °C; ^{1}H NMR (90 MHz, $CDCl_3$, 24 °C) δ/ppm 8.20−7.95 (2H, m), 7.90−7.40 (6H, m); IR (KBr) 2244, 1474, 1186, 1066, 760, 746 cm^{-1}; FD-MS m/z (relative intensity) 350 (M^+, 100), 352 (M^+, 67). Anal. Calcd for $C_{18}H_8N_4Cl_2$: C, 61.56; H, 2.30; N, 15.95. Found: C: 61.70, H, 2.42; N, 15.93. Data of **3**: mp 222−224 °C; ^{1}H NMR (300 MHz, $CDCl_3$, 24 °C) δ/ppm 7.97 (2H, dd, $J = 7.5, 1.5$ Hz), 7.91 (2H, dd, $J = 7.5, 1.5$ Hz), 7.78 (2H, ddd, $J = 7.5, 7.5, 1.5$ Hz), 7.67 (2H, dd, $J = 7.5, 7.5, 1.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$, 24 °C) δ/ppm 45.77, 109.77, 121.50, 126.50, 127.97, 130.94, 131.03, 133.47; IR (KBr) 2248, 1482, 1456, 762, 724 cm^{-1}; UV (MeCN) λ_{max} 301 (log ϵ 3.74), 280 sh (4.07), 272 (4.11), 212 (4.61); EI-MS m/z (relative intensity) 280 (M^+, 100), 253 (85), 215 (97). Anal. Calcd for $C_{18}H_8N_4$: C, 77.13; H, 2.89; N, 19.99. Found: C, 77.24; H, 3.04; N, 20.04.

X-ray Analyses. All data collection was performed on a Rigaku Mercury CCD camera apparatus (Mo−Kα radiation, λ= 0.71069 Å, 50 kV, 50 mA) at 203 K.

1: $C_{42}H_{36}N_2O$, M 584.76, colorless rod, 0.6 × 0.1 × 0.05 mm, orthorhombic $P2_12_12_1$, $a = 10.4511(4)$, $b = 14.0601(7)$, $c = 20.771(1)$ Å, $V = 3052.2(3)$ Å^3, ρ ($Z = 4$) = 1.272 g cm^{-1}. Numerical absorption correction was applied ($\mu = 0.76$ cm^{-1}). The structure was solved by the direct method and refined by the full-matrix least-squares method on F with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. The final R and Rw values are 0.044 and 0.049 for 407 parameters and 2835 reflections with $I > 3\sigma$I (independent reflections, 3625; $2\theta_{max} = 53.5°$). The GOF indicator is 1.20. Residual electron density is 0.16 e Å^{-3}.

2: $C_{32}H_{28}N_4$, M 468.60, colorless rod, 0.6 × 0.2 × 0.05 mm, monoclinic $P2_1/c$, $a = 16.603(1)$, $b = 7.8501(6)$, $c = 19.920(4)$ Å, $\beta = 94.247(4)°$, $V = 2589.2(6)$ Å^3, ρ ($Z = 4$) = 1.202 g cm^{-1}. Numerical absorption correction was applied ($\mu = 0.72$ cm^{-1}). The structure was solved by the direct method and refined by the full-matrix least-squares method on F with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. The final R and Rw values are 0.062 and 0.074 for 325 parameters and 2716 reflections with $I > 3\sigma$I (independent reflections, 5597; $2\theta_{max} = 53.5°$). The GOF indicator is 1.64. Residual electron density is 0.17 e Å^{-3}.

3: $C_{18}H_8N_4$, M 280.29, colorless rod, 0.5 × 0.15 × 0.1 mm, monoclinic $C2/c$, $a = 16.908(4)$, $b = 12.786(3)$, $c = 7.050(1)$ Å, $\beta = 115.043(6)°$, $V = 1380.8(5)$ Å^3, ρ ($Z = 4$) = 1.348 g cm^{-1}. Numerical absorption correction was applied ($\mu = 0.84$ cm^{-1}). The structure was solved by the direct method and refined by the full-matrix least-squares method on F with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. The final R and Rw values are 0.042 and 0.069 for 100 parameters and 1208 reflections with $I > 3\sigma$I (independent reflections, 4432; $2\theta_{max} = 59.8°$). The GOF indicator is 2.37. Residual electron density is 0.18 e Å^{-3}.

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Supporting Information Available: ORTEP drawings and structural data for the X-ray analyses (positional and thermal parameters; bond distances and angles) of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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