Synthesis, Isolation, and Characterization of Diels–Alder Adducts between 1,4-Dialkoxyanthracenes and Maleic Anhydride

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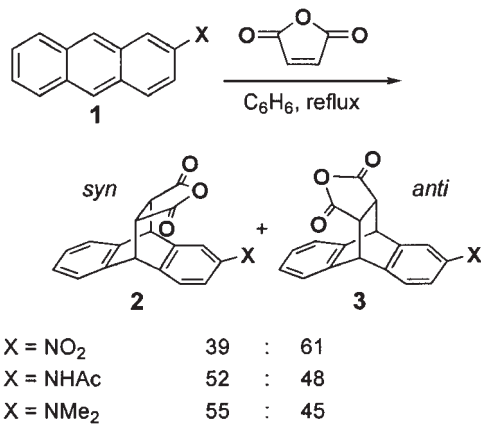
In the Diels–Alder reaction of 1,4-dialkoxyanthracenes and maleic anhydride, which can afford *syn*- and *anti*-cycloadducts, the bridgehead methine proton of the cycloadducts has proved to be a useful probe for determining *syn*/*anti* selectivity, as supported by isolation of diastereomers, ^{1}H NMR spectroscopy, and X-ray analysis. In the case of methoxy and propoxy substituents, a slight *anti*-preference was observed, on the other hand, the reaction of 1,4-bis(benzyloxy)anthracene gave a small *syn*-preference. Theoretical calculations of transition states of 1,4-dimethoxyanthracene and maleic anhydride showed no stereochemical preference. From UV–vis spectra, the formation of charge transfer complexes of anthracenes and maleic anhydride is possible.

The Diels–Alder (DA) reaction is one of the fundamental organic reactions. It is well known that anthracenes give thermal and photochemical DA reactions with alkenes readily and can easily be reverted to the starting anthracene by a retro-DA reaction. Recently, some groups have been reporting diastereoselective DA reactions of anthracenes that possess a chiral group at the 9-position and proposing anthracene-based templates for new asymmetric DA/retro-DA strategies.[1] Even if anthracene does not have any chiral groups, the introduction of substituent groups on the 1-, 2-, 3-, and/or 4-positions of the anthracene nucleus can permit the formation of two *syn*- and *anti*-diastereomers (throughout this paper, *syn* and *anti* are used in the sense that the substituents on the same side as succinic anhydride are *syn*, the others *anti*) in the DA reaction.[2] In general, the importance of steric, orbital, and electrostatic factors to control stereoselectivity has been recognized.[3] With respect to anthracenes bearing substituents except on the 9- and/or 10-positions, there have been only a few studies on stereochemical DA reactions. One of the most representative experiments is the DA reaction of 2-substituted anthracenes (**1**), in which the substituent was varied from the strongly electron-donating dimethylamino group to the strongly electron-withdrawing nitro group, with maleic anhydride, reported by Kaplan and Conroy (Scheme 1).[4] They reported that when the substituent had electron-donating ability, the *syn*-cycloadduct **2** became slightly dominant. In the case of nitro group, little *anti*-preference of **3** was observed. They thought that the order of reactivity could be attributed to the difference in electrostatic effects between the anthracene and maleic anhydride in the transition state. The above result prompted us to investigate the behavior of the anthracenes containing alkoxy groups at the 1- and 4-positions, as dienes, in order to confirm Conroy's hypothesis about the stereoselectivity of DA adducts between 1,4-dialkoxyanthracenes and maleic anhydride from the viewpoint of the electrostatic effects and to survey other factors, except for the foregoing hypothesis. In recent years, as a part of our study about triptycenes and iptycenes,[5] we have been synthesizing some 1,4-dialkoxy anthracenes, which contain strong electron-donating alkoxy groups and should be better dienes. In this paper, we describe the results of our experimental investigations on the Diels–Alder reaction of 1,4-dimethoxy-, 1,4-dipropoxy-, and 1,4-bis(benzyloxy)anthracenes **4a–c** (Chart 1) with maleic anhydride. We also report the structural characterization of the DA adducts accomplished by X-ray analysis and ^{1}H NMR spectroscopy, and theoretical investigations.



Scheme 1.

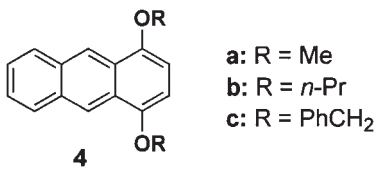


Chart 1.

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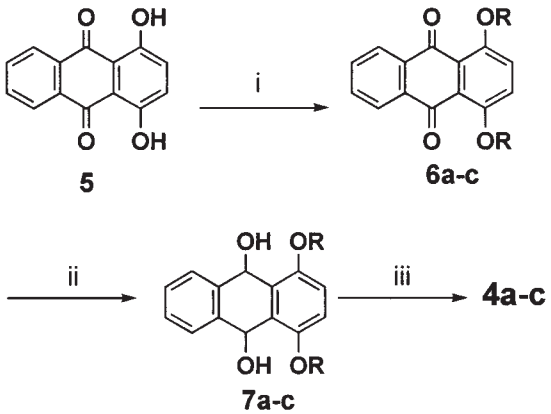
Results and Discussion

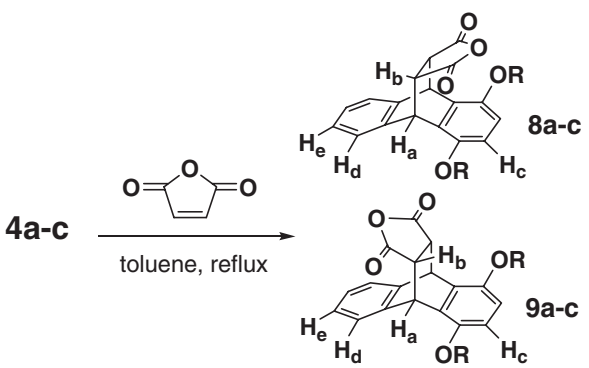
The anthracenes **4a** and **4b**,**c** were prepared by the modified methods of Klanderman[6] and Lepage,[7] respectively (Scheme 2). Etherification of quinizarin (**5**) in the presence of K_2CO_3 yielded anthraquinones **6a–c** in 83–97% yields. Reduction of **6a–c** with $NaBH_4$ in MeOH–THF followed by careful neutralization to pH 7 with acetic acid gave diols **7a–c** as transient intermediates. Treatment of **7a–c** with 5–7 M HCl in THF at 40 °C under air afforded anthracenes **4a–c** in 35–40% two-step yields. This procedure did not need a sequence of isolation of anthrone, reduction, and acidification.

The first DA reaction performed was that of **4a**. The reaction of **4a** with maleic anhydride (1.5 equiv) in refluxing toluene under an inert atmosphere for 6 h furnished a mixture of two diastereoisomers, the *syn*-cycloadduct **8a** and *anti*-cycloadduct **9a** in an isolated yield of 92%, accompanied by a complete loss of **4a** (Table 1).



Scheme 2. Reagents and conditions: i, (a) TosOMe, K_2CO_3, *o*-dichlorobenzene, reflux, 1 h, 83%; (b) PrBr, K_2CO_3, DMF, 100 °C, 6 h, 97%; (c) $PhCH_2Cl$, K_2CO_3, DMF, 100 °C, 6 h, 83%; ii, $NaBH_4$, MeOH–THF, 0 °C, 30 min, quantitative; iii, (a) 7 M HCl, THF, 40 °C, 2 h, 40%; (b) 5 M HCl, THF, 40 °C, 4 h, 37%; (c) 5 M HCl, THF, 40 °C, 4 h, 35%.

Table 1. Preparation of Cycloadducts **8** and **9**



Substrate	Compound	R	**8**/**9**	Yield/%[a)]
4a	**8a** + **9a**	Me	45:55	92
4b	**8b** + **9b**	*n*-Pr	43:57	87
4c	**8c** + **9c**	$PhCH_2$	57:43	86

a) Isolated yield.

The two diastereomers **8a** and **9a** in the mixture were distinguishable by ^{1}H NMR spectroscopy. Thus, the ^{1}H NMR spectrum, taken of the crude mixture, distinctly showed the signals of not only bridgehead methine H_a at δ 5.30 and δ 5.34 (two broad singlets), but also benzene H_d at δ 7.35 and δ 7.41 (two double doublets), though chemical shifts of another methine H_b (at δ 3.47–3.48 as two singlets), benzene H_c (at δ 6.67–6.69 as two singlets), H_e (at δ 7.17–7.20 as multiplet), and methyl groups (at δ 3.81–3.82 as two singlets) were almost identical. Several attempts to separate **8a** and **9a** by column chromatography and recrystallization were unsuccessful. However, we were able to isolate small amounts of both **8a** and **9a** by taking advantage of the difference in their solubility in Et_2O. Thus, by repetition of washing the mixture of **8a** and **9a** with Et_2O, the residue enriched **8a**, while the filtrate enriched **9a** (Fig. 1). Finally, they were purified by recrystallization from toluene. NOE studies did not lead to the determination of the *syn*- and *anti*-structures because both compounds provide the same correlations such as between H_a and H_b, between H_a and H_d, and between H_d and H_e (Fig. 2). Further, the H_b in **8a** did not display an NOE interaction with H_d. However, we succeeded in X-ray analysis of both **8a** and **9a**. The X-ray structures established the stereochemical relationships unambiguously (Fig. 3). Thus, the molecular structures revealed that the configuration of the component that was more soluble in Et_2O was *anti*-**9a** (Fig. 3b),[8] although the stereochemistry of another component was *syn*-**8a** (Fig. 3a). In both molecules, methoxy groups in the solid state lay in the benzene plane. These conformations were similar to the minimum energy *syn*-planar conformation[9] of 1,4-di-

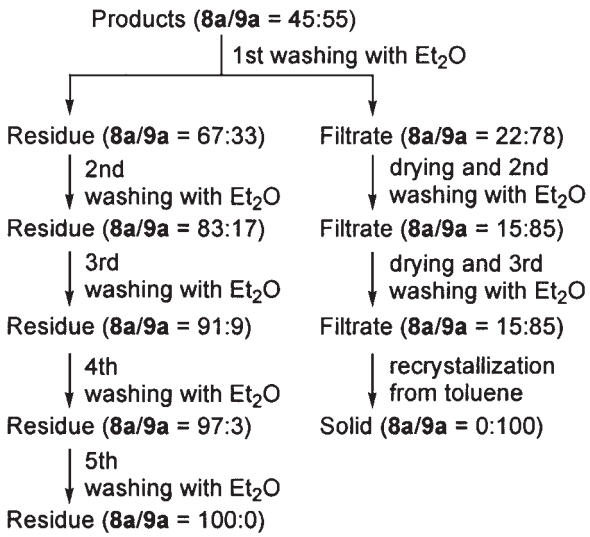


Fig. 1. Schematic diagram showing separation of **8a** and **9a**.

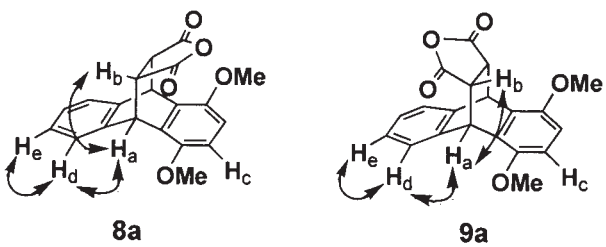


Fig. 2. NOE correlations of **8a** and **9a**.

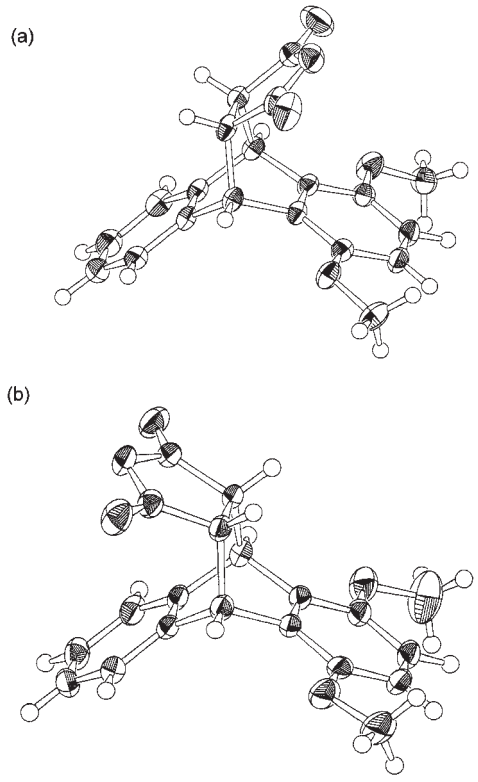


Fig. 3. Molecular structures of (a) **8a** and (b) **9a**.

methoxybenzene and our X-ray analysis[10] of 1,4-dimethoxyanthracene. When **8a** and **9a** were heated in toluene at reflux for a longer period, such as more than 24 h, no isomerization was observed. This showed that the DA adducts **8a** and **9a** were thermodynamically stable and that at the temperature applied no retro-DA reaction occurred.

On the basis of the X-ray analysis, the characterization of the *syn*- and *anti*-adducts was confirmed by ^{1}H spectroscopy (Table 2). Thus, the signals of δ 5.30 and δ 5.34 were assigned to the methine H_a of *anti*-**9a** and *syn*-**8a**, respectively, and similarly the signals of benzene H_d of *anti*-**9a** and *syn*-**8a** were assigned to δ 7.35 and δ 7.41, respectively. The difference in the chemical shifts of H_d (between δ 7.35 and δ 7.41) can be attributed to the ^{1}H NMR anisotropy effect arising from different spatial arrangements of the carbonyl oxygen atom in the molecules. On the other hand, the difference in the chemical shifts of H_a (between δ 5.30 and δ 5.34) can be explained by the van der Waals interaction between H_a and the oxygen atom in MeO. Thus, the mean intramolecular distances H_a···OMe for **8a** and **9a** in the crystals were 2.54 and 2.53 Å, respectively, indicating **9a** had a slightly stronger van der Waals repulsion. By comparing the integral ratios of H_a, H_c, and H_d protons, **8a**/**9a** ratio of 45:55 was obtained, exhibiting a slight *anti*-preference. This result is different from Conroy's result of the anthracenes with an electron-donating group at the 2-position (Scheme 1). At this point we were thinking that the steric effects of methoxy substituents surpassed the electronic ones. This idea was denied by later considerations.

We recognized the bridgehead methine H_a signals in **8** and **9** as a useful probe for not only the obvious distinctions between *syn* and *anti* but also the determination of *syn*/*anti* selectivity. Thus, from a ^{1}H NMR spectrum of a mixture of **8** and **9**, the two H_a signals at lower and higher fields can be assigned to *syn*-**8** and *anti*-**9**, respectively, and the *syn*/*anti* ratio can be obtained from the integral ratios. In order to confirm this analytical criterion, we tried to apply it to characterize **8b** and **9b** as well as **8c** and **9c**.

The DA reaction of **4b**,**c** and maleic anhydride yielded **8b**/**9b** and **8c**/**9c** mixtures in yields of 87 and 86%, respectively (Table 1). We could not separate either mixture. This differed from the case of the mixture of **8a** and **9a**. From the ^{1}H NMR spectra of their mixtures, the bridgehead H_a signals in **8b** and **9b** were assigned to δ 5.35 and δ 5.30, respectively, and those of **8c** and **9c** were assigned to δ 5.42 and δ 5.29, respectively (Table 2). In the case of the mixture of **8b** and **9b**, we were able to assign H_c (**8b**: δ 6.65 and **9b**: δ 6.64) and H_d (**8b**: δ 7.40 and **9b**: δ 7.34) protons, by considering the comparison of chemical shifts of **8a** and **9a**. We also regarded the chemical shifts of H_d in **8b** and **9b** as comparable to those in **8a** and **9a** (**8a**: δ 7.41 and **9a**: δ 7.35), respectively. In the case of the mixture of **8c** and **9c**, we assumed that the signals of δ 3.52 and δ 3.28 were assigned to the H_b protons of **8c** and **9c**, respectively, and that the signals of δ 6.70 and δ 6.74 were assigned to the H_c protons of **8c** and **9c**, respectively. The finding that the H_b signal in **9c** was shifted higher than that in **9a** or **9b** would indicate shielding by the benzene ring, which was attached to the substituent in **9c**. From the integral ratio of H_a, we estimated the *syn*/*anti* selectivity of **8b**/**9b** and **8c**/**9c** to be 43:57 and 57:43, respectively, meaning that the former has a slight *anti*-preference and the latter has, interestingly, a little *syn*-preference.

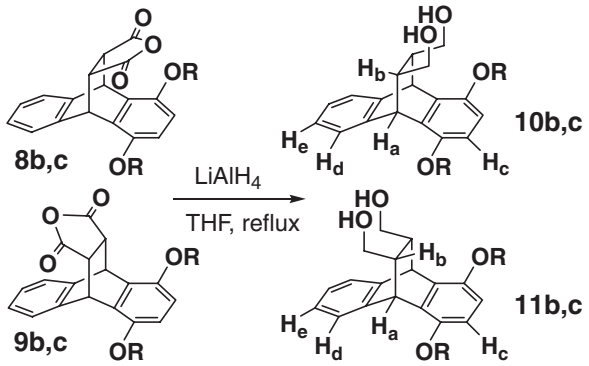
Because we failed in separating the mixtures of **8b** and **9b** as well as **8c** and **9c**, we tried to transform them into the molecules that could be easily separated in order to establish characterization. We succeeded in isolating their reduction products. Thus,

Table 2. 500 MHz ^{1}H NMR Spectral Data (δ in ppm) for **8a–c**, **9a–c**, **10b**,**c**, and **11b**,**c** in $CDCl_3$

	8a[a]	**9a**[a]	**8b**[b]	**9b**[b]	**8c**[b]	**9c**[b]	**10b**[a]	**11b**[a]	**10c**[a]	**11c**[a]
H_a	5.34 brs	5.30 brs	5.35 brs	5.30 brs	5.42 brs	5.29 brs	4.75 brs	4.63 brs	4.80 brs	4.66 brs
H_b	3.48 brs	3.47 brs	3.47–3.49 m		3.52 brs	3.28 brs	2.33–2.35 m	2.34–2.36 m	2.33–2.36 m	2.25–2.27 m
H_c	6.69 s	6.67 s	6.65 s	6.64 s	6.70 s	6.74 s	6.58 s	6.58 s	6.65 s	6.65 s
H_d	7.41 dd (3.2, 5.2)[d]	7.35 dd (3.2, 5.2)[d]	7.40 dd (3.2, 5.2)[d]	7.34 dd (3.2, 5.2)[d]	NA[c]	NA[c]	7.31 dd (3.2, 5.2)[d]	7.23 dd (3.2, 5.2)[d]	7.31 dd (3.2, 5.2)[d]	7.23 dd (3.2, 5.2)[d]
H_e	7.18 dd (3.2, 5.4)[d]	7.19 dd (3.2, 5.4)[d]	7.16–7.20 m		7.16–7.20 m		7.12 dd (3.2, 5.4)[d]	7.08 dd (3.2, 5.4)[d]	7.12 dd (3.2, 5.4)[d]	7.09 dd (3.2, 5.4)[d]

a) Isolated compounds. b) Assigned components in the mixture. c) NA = not assigned because of overlapping of benzyl protons. d) J in Hz.

Table 3. Preparation of Diols **10** and **11**



Substrate	Compound	R	**10**/**11**	Yield/%[a)]
8b + **9b**	**10b** + **11b**	*n*-Pr	43:57	96
8c + **9c**	**10c** + **11c**	$PhCH_2$	57:43	91

a) Crude yield.

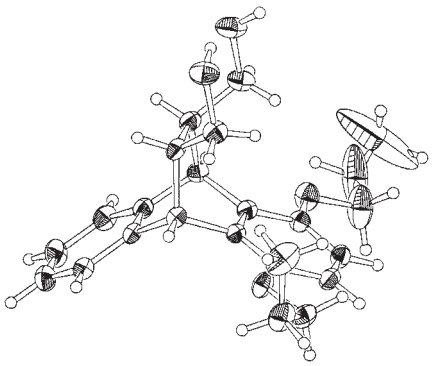


Fig. 4. Molecular structure of **10b**.

diols **10b** and **11b** were prepared by reduction of a mixture of **8b** and **9b** with $LiAlH_4$ in THF for 4 h in 96% yield, while **10c** and **11c** were obtained from a mixture of **8c** and **9c** in 91% yield (Table 3). The ratios of **10b**/**11b** and **10c**/**11c**, which were determined from the integral ratios of H_a in the state of crude mixtures, were 43:57 (H_a: δ 4.75 vs δ 4.63, Table 2) and 57:43 (H_a: δ 4.80 vs δ 4.66), respectively. These values were, of course, the same as those of **8b**/**9b** and **8c**/**9c**, respectively. In the case of **10b**/**11b**, the ratio was supported by the integral ratio of H_d protons. Purification by column chromatography of the former mixture afforded **10b** and **11b** independently, and purification of the latter mixture gave **10c** and **11c** separately. We succeeded in X-ray analysis of one component, with a higher R_f value on silica gel TLC developed by (2:1) $CHCl_3$–AcOEt, between **10b** and **11b** that had the H_a signals of δ 4.75. The molecule proved to be **10b** by displaying *syn*-configuration (Fig. 4). It was also observed that except for the terminal methyl group of the propoxy group, two methylene groups lay in the benzene plane. Since the stereochemistry of one component with a higher R_f value turned out to be **10b**, another component with a lower R_f value was defined as **11b** unequivocally. Therefore assignment of ^{1}H NMR data for both diols was established (Table 2). Even in the case of the reduction products, it was confirmed that the bridgehead H_a signals at lower and higher fields can be assigned to the *syn*- and *anti*-configurations, respectively, in analogy with the case of **8b** and **9b**. NOE studies

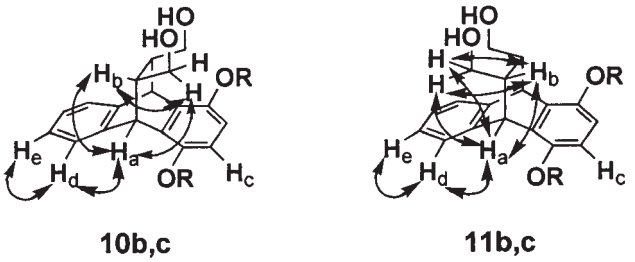


Fig. 5. NOE correlations of **10b**,**c** and **11b**,**c**.

did not furnish valuable information about the identification of *syn* and *anti* on account of the same NOE correlations because neither NOE correlation between H_b and H_d nor between methylene groups and H_d was observed, as shown in Fig. 5. As for **10c** and **11c**, the assignment of proton signals were made on the basis of chemical shifts of **10b** and **11b** (Table 2). Thus, we noticed the identity of the chemical shifts of H_d (**10b**: δ 7.31, **10c**: δ 7.31, **11b**: δ 7.23, and **11c**: δ 7.23) and H_e (**10b**: δ 7.12, **10c**: δ 7.12, **11b**: δ 7.08, and **11c**: δ 7.09) protons, which were not geographically influenced by the substituent groups at the 1- and 4-postions. Further, **10c** defined above had a higher R_f value on silica gel TLC developed by (2:1) $CHCl_3$–AcOEt than **11c**, and this propensity is consistent with the observation that *syn*-**10b** had a higher R_f value compared with *anti*-**11b**. Therefore, we judged our characterization of **10c** and **11c** valid. The bridgehead methine H_a signals of **10c** and **11c** were assigned to δ 4.80 and δ 4.66, respectively. From the above findings, we concluded that the assignment method for determining *syn*- and *anti*-structure by ^{1}H spectroscopy was reasonable. This will be instructive to characterization of other DA adducts between 1,4-dialkoxyanthracenes and maleic anhydride.

We found that DA reaction of 1,4-dialkyloxyanthracene **4a**,**b** and maleic anhydride afforded a small *anti*-preference, on the other hand, DA reaction of 1,4-bis(benzyloxy)anthracene **4c** with maleic anhydride resulted in a small *syn*-preference. It seems unreasonable to assume that steric effects of the substituent groups play a part in direct determination of *syn*/*anti* selectivity. We thought that the substituent groups in anthracenes **4a**–**c** were located in the place where the DA reaction was not prevented, therefore there was hardly any steric repulsion between the substituent groups and maleic anhydride. Then, we carried out a conformational search for **4b** and **4c** using the molecular mechanics mode and examined energies for each of the different conformers. The lowest-energy conformers for **4b** and **4c** are shown in Fig. 6. It can be seen that, although **4b** has a planar conformation, in the case of **4c**, two methylene parts of the benzyl groups are not only *anti* but almost perpendicular to anthracene, and the phenyl rings are apart from the anthracene. The special conformation of **4c** may relate to the different result in the *syn*/*anti* selectivity. In addition, if Conroy's interpretation on the electrostatic interactions (Scheme 1) is right, we had to gain the results of all *syn*-preference. These situations suggest that we have to consider other factors to understand the *syn*/*anti* selectivity.

In order to analyze the origin of the *syn*/*anti* selectivity of the DA adducts, we carried out a computational evaluation of Frontier orbitals (FOs) of **4a** and maleic anhydride, and the transition structures (TSs) of **8a** and **9a** using B3LYP/6-

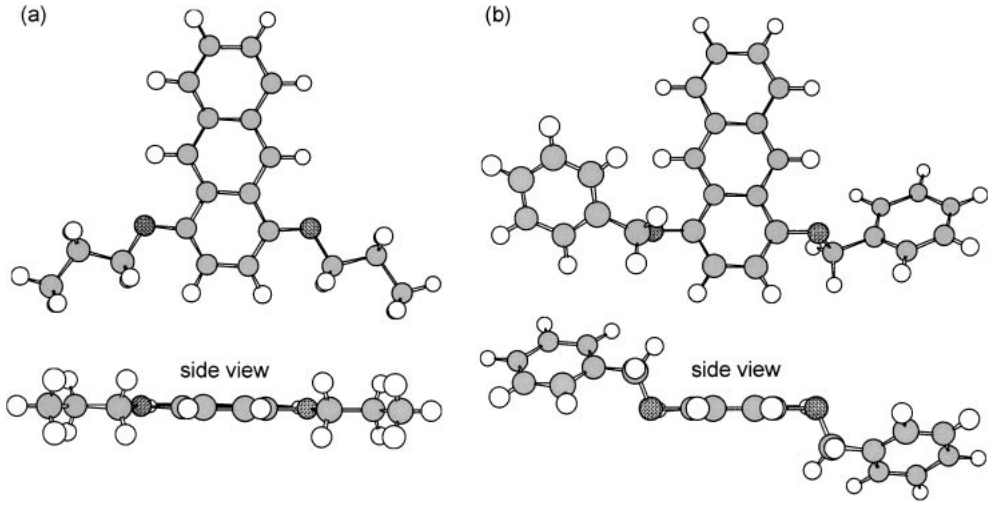


Fig. 6. Top and side views of the lowest-energy conformers for (a) **4b** and (b) **4c**, examined by the molecular mechanics conformation search.

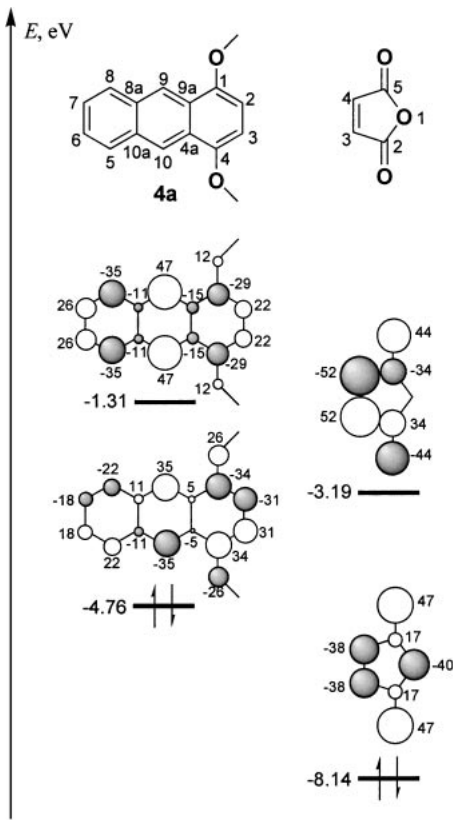


Fig. 7. The FOs of **4a** and maleic anhydride. Numbers near levels are the B3LYP orbital energies in eV and numbers near the atomic orbitals (AOs) are STO3G//B3LYP coefficients. The AO coefficients are given in units of 10^{-2}.

31G(d) calculations. The FOs are depicted in Fig. 7 and show clearly that the interaction between the HOMO of **4a** and the LUMO of maleic anhydride is primary and that the largest atomic orbital (AO) coefficients of **4a** and maleic anhydride are the 9,10-positions and the 3,4-positions, respectively. The FOs of **4a** and maleic anhydride could not explain the remarkable difference between the *syn*- and *anti*-orientations, as illustrated in Fig. 8. Thus, the AO coefficients at C4a, C9a, C8a, and C10a of the HOMO of **4a** are so small that the secondary orbital interactions[11] (SOIs) of C4a/C9a (HOMO)···C2/C5 (LUMO) in the *syn*-orientation should be comparable to that of C8a/C10a (HOMO)···C2/C5 (LUMO) in the *anti*-orientation. We have optimized the TSs as shown in Fig. 9, which were characterized by a single negative frequency. The degree of bond formation was synchronous and the lengths of the incipient bonds were essential identical (2.203 Å in *syn*-orientation and 2.207 Å in *anti*-orientation). The degree of bending (e.g., dihedral angle) was similar in magnitude in both the *syn*- and *anti*-orientation. Further, our calculations predicted that the relative difference in activation enthalpies of two possible TSs was 0.06 kcal mol^{-1} (*anti*-mode was faintly higher), indicating their values are substantially identical. This result means that the sum of contributions from steric effects, SOIs, electrostatic interactions, and other interactions, which are all associated with both TSs, are the same in the *syn*- and *anti*-orientation. Then, in order to evaluate Conroy's result at the same computational level, we have calculated the TSs of formation of the *syn*- and *anti*-adducts derived from 2-nitoroanthracene and 2-dimethylaminoanthracene, respectively. Our calculation indicated that the *anti*-TS for 2-nitroanthracene was 0.31 kcal mol^{-1} more stable

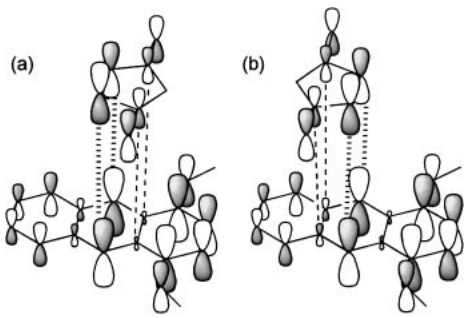


Fig. 8. The HOMO–LUMO interactions between **4a** and maleic anhydride in (a) *syn*-orientation and (b) *anti*-orientation. Bold dashes specify the primary interactions while dashed lines refer to the SOIs.

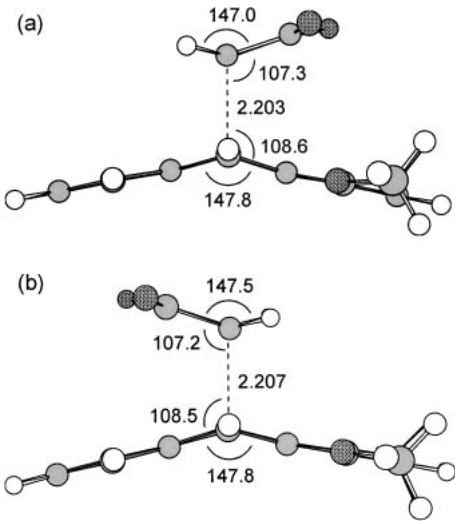


Fig. 9. Calculated transition structures associated with the formation of (a) *syn*-**8a** and (b) *anti*-**9a**, together with selected geometrical parameters.

than the *syn*-TS, and that the *anti*-TS for 2-dimethylaminoanthracene was 0.57 kcal mol^{-1} higher than the *syn*-TS. These energetic differences correspond to an *anti*-preference for 2-nitroanthracene and a *syn*-preference for 2-dimethylaminoanthracene, and are in good agreement with Conroy's experimental result that reflects the contribution of the electrostatic interaction. We therefore should consider another factor that influences the stereochemical course of the DA reactions of 1,4-dialkoxyanthracenes as well as is not involved in TS.

In regard to the DA reaction of anthracene with an electron-deficient dienophile, a mechanism via the formation of a charge transfer (CT) complex has been proposed.[12] The importance of the CT complex formation in the [4 + 2] cycloaddition has been also documented.[13,14] In our case, a change in solution color with reaction time was observed. The color was initially reddish-orange and gradually turned colorless as the reaction proceeded, suggesting the formation and disappearance of the CT complex. Treatment of **4a**–**c** with maleic anhydride in chloroform at room temperature led to the rapid formation of CT complexes, which could not be isolated, with new UV–vis absorption bands at 450–500 nm. The above results clearly indicate that the DA reactions of 1,4-dialkoxyanthracenes with maleic anhydride proceed via the formation of CT complexes. Furthermore, judging by the consideration of the CT complex and the above result of the theoretical calculations, the origin of the *syn*/*anti* selectivity of the products could be the *syn*/*anti* ratios of orientation of **4a**–**c** and maleic anhydride in the CT complexes. Recently, Suárez and Sordo have reported that the pre-reactive van der Waals complexes may play a decisive role in determining the stereochemical outcome of DA reactions,[15] indicating the importance of the stereochemical composition in pre-reactive molecular complexes. Therefore, we believe the DA reaction of 1,4-dialkoxyanthracenes and maleic anhydride proceeds by not a direct pathway (Path b, Fig. 9) but a two-step route via a CT complex (Path a, Fig. 10). We are currently examining the effects of varying the substituent group of anthracene in order to gain a clearer understanding of the relation between the CT complex and *syn*/*anti* selectivity.

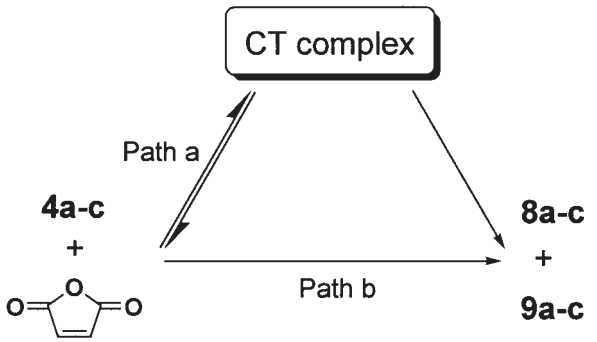


Fig. 10. Putative reaction mechanism.

In conclusion, we found that the bridgehead proton of cycloadducts was an effective probe for investigating the stereochemistry of the DA reaction between 1,4-dialkoxyanthracenes and maleic anhydride, which was established by the isolation of diastereomers, ^{1}H NMR spectroscopy, and X-ray analysis. The stereochemical behavior of the products showed that the *syn*/*anti* ratios were close to 1:1 but the values fluctuated according to the substituent groups. In the case of methoxy and propoxy derivatives, a slight *anti*-preference was observed. However, the DA reaction of 1,4-bis(benzyloxy)anthracene resulted in a small *syn*-preference. From computational studies, the difference in reaction courses in the *syn*- and *anti*-orientation was not detected. The formation of pre-reactive CT complexes was observed, and it was considered that the *syn*- and *anti*-arrangement of 1,4-dialkoxyanthracenes and maleic anhydride in the CT complexes might determine the *syn*/*anti* ratios of the products.

Experimental

General. THF and DMF were distilled from $LiAlH_4$ and CaH_2, respectively, prior to use. Commercially available reagents were used as supplied unless otherwise stated. All reactions were carried out under a nitrogen atmosphere unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} 0.25 mm aluminium plates, and components were visualized by UV light or by iodine vapor. Column chromatography was performed on Wako silica gel C-300 (45–75 μm, 300 mesh). Mp's were determined on a Yanaco Melting Point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX500 FT spectrometer at 500 and 126 MHz, respectively. Chemical shifts were referenced to TMS. IR spectra were recorded on a Shimadzu FTIR-8400 spectrometer as KBr pressed pellets. Electron impact mass spectra were obtained at 70 eV on a Shimadzu QP-1000EX. Elemental analysis was carried out on a Yanaco MT-5 CHN corder.

General Procedure for the Preparation of 1,4-Dialkoxyanthracene 4a–c. A mixture of quinizarin (10.0 g, 41.6 mmol), K_2CO_3 (17.3 g, 125 mmol), and an excess (5 equiv) of electrophile was heated at reflux for 1 h in *o*-dichlorobenzene (70 mL) for preparation of **6a** or at 100 °C for 6 h in dry DMF (30 mL) for preparation of **6b**,**c**. After conventional work-up and purification by recrystallization, anthraquinones **6a**–**c** were treated with $NaBH_4$ (5 equiv) in (2:1) MeOH–THF at 0 °C for 30 min. The reaction mixtures were neutralized with acetic acid, then extracted with AcOEt, washed with brine, and dried over Na_2SO_4. After evaporation of the solvent, 9,10-dihydroxy-9,10-dihydroanthracenes **7a**–**c** were

obtained as brown oils in quantitative yields. Without purification, **7a–c** were dissolved in THF (100 mL) and 7 M (for **7a**) or 5 M (for **7b**,**c**) HCl (50 mL) was added. The mixtures were then stirred at 40 °C for 2 h (for **7a**) or 4 h (for **7b**,**c**) under air. After neutralization with 5 M NaOH, the solutions were extracted with $CHCl_3$. The extracts were washed with brine and dried over Na_2SO_4. Purification by column chromatography ($CHCl_3$–haxane) gave **4a–c** as yellow solids in yields of 40% from **7a**, 37% from **7b**, and 35% from **7c**.

1,4-Dimethoxyanthracene (4a).[16] Mp 134–136 °C (lit.[4] 134–136 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.03 (s, 6H, 2OCH_3), 6.61 (s, 2H, 2-H, 3-H), 7.48 (dd, J = 3.1, 6.4 Hz, 2H, 6-H, 7-H), 8.04 (dd, J = 3.1, 6.4 Hz, 2H, 5-H, 8-H), 8.77 (s, 2H, 9-H, 10-H).

1,4-Dipropoxyanthracene (4b). Mp 66–67 °C; IR (KBr) 2968, 2936, 1622, 1578, 1456 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18 (t, J = 7.4 Hz, 6H, 2CH_2CH_3), 1.98–2.05 (m, 4H, 2CH_2C$H_2$$CH_3$), 4.12 (t, J = 6.6 Hz, 4H, 2OC$H_2$$CH_2$), 6.59 (s, 2H, 2-H, 3-H), 7.47 (dd, J = 3.2, 6.4 Hz, 2H, 6-H, 7-H), 8.05 (dd, J = 3.2, 6.4 Hz, 2H, 5-H, 8-H), 8.80 (s, 2H, 9-H, 10-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.92, 22.78, 69.84, 101.90, 120.72, 125.33, 125.75, 128.55, 131.36, 148.68; MS (EI) m/z (relative intensity) 294 (M^+, 93), 209 (100). Anal. Calcd for $C_{20}H_{22}O_2$: C, 81.60; H, 7.53%. Found: C, 81.33; H, 7.41%.

1,4-Bis(benzyloxy)anthracene (4c). Mp 153–158 °C (lit.[5] 149–150 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.28 (s, 4H, 2OCH_2Ph), 6.67 (s, 2H, 2-H, 3-H), 7.37–7.40 (m, 2H, 2PhH), 7.44–7.59 (m, 10H, 6-H, 7-H, 8PhH), 8.04 (dd, J = 3.2, 6.4 Hz, 2H, 5-H, 8-H), 8.86 (s, 2H, 9-H, 10-H).

General Procedure for Diels–Alder Reaction of 1,4-Dialkoxyanthracene 4 with Maleic Anhydride. A mixture of **4a–c** (1.0 mmol) and maleic anhydride (1.5 mmol) in toluene (3 mL) was heated at reflux for 6 h. After evaporation of the solvent and drying under vacuum, the residue was well ground and observed with ^{1}H NMR to determine diastereoselectivity.

(11*R,15*S**)-1,4-Dimethoxy-9,10,11,15-tetrahydro-9,10[3′,4′]-furanoanthracene-12,14-diones (8a and 9a).** **8a**/**9a** = 45:55. Purified by recrystallization from toluene to give a mixture of **8a** and **9a** as a white solid (309 mg, 0.92 mmol, 92%), mp 230–232 °C. The diastereoisomers were inseparable by column chromatography and were characterized as a mixture. IR (KBr) 2949, 1782, 1497, 1261, 1078, 928 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.47 (brs, 2H, 2CHCH(C=O), **9a**), 3.48 (brs, 2H, 2CHCH(C=O), **8a**), 3.81 (s, 6H, 2OCH_3, **8a**), 3.82 (s, 6H, 2OCH_3, **9a**), 5.30 (brs, 2H, 2CHCH(C=O), **9a**), 5.34 (brs, 2H, 2CHCH(C=O), **8a**), 6.67 (s, 2H, 2-H, 3-H, **9a**), 6.69 (s, 2H, 2-H, 3-H, **8a**), 7.16–7.20 (m, 2H, 6-H, 7-H, **8a** and **9a**), 7.35 (dd, J = 3.2, 5.2 Hz, 2H, 5-H, 8-H, **9a**), 7.41 (dd, J = 3.2, 5.2 Hz, 2H, 5-H, 8-H, **8a**); MS (EI) m/z (relative intensity) 223 (95), 238 (100), 336 (M^+, 37). Anal. Calcd for $C_{20}H_{16}O_5$: C, 71.42; H, 4.79%. Found: C, 71.78; H, 4.89%.

(11*R,15*S**)-1,4-Dipropoxy-9,10,11,15-tetrahydro-9,10[3′,4′]-furanoanthracene-12,14-diones (8b and 9b).** **8b**/**9b** = 43:57. Purified by column chromatography ($CHCl_3$–hexane–AcOEt, 10:5:1) to give a mixture of **8b** and **9b** as a white solid (341 mg, 0.87 mmol, 87%), mp 184–186 °C. The diastereoisomers were inseparable by column chromatography and were characterized as a mixture. IR (KBr) 2964, 1782, 1497, 1265, 1076, 934 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06–1.10 (m, 6H, 2CH_2CH_3, **8b** and **9b**), 1.81–1.87 (m, 4H, 2CH_2C$H_2$$CH_3$, **8b** and **9b**), 3.47–3.49 (m, 2H, 2CHCH(C=O), **8b** and **9b**), 3.82–3.96 (m, 4H, 2OC$H_2$$CH_2$, **8b** and **9b**), 5.30 (brs, 2H, 2CHCH(C=O), **9b**), 5.35 (brs, 2H, 2CHCH(C=O), **8b**), 6.64 (s, 2H, 2-H, 3-H, **9b**), 6.65 (s, 2H, 2-H, 3-H, **8b**), 7.16–7.20 (m, 2H, 6-H, 7-H, **8b** and **9b**), 7.34 (dd, J = 3.2, 5.2 Hz, 2H, 5-H, 8-H, **9b**), 7.40 (dd, J = 3.2, 5.2 Hz, 2H, 5-H, 8-H, **8b**); MS (EI) m/z (relative intensity) 209 (80), 294 (100), 392 (M^+, 57). Anal. Calcd for $C_{24}H_{24}O_5$: C, 73.45; H, 6.16%. Found: C, 73.37; H, 6.26%.

(11*R,15*S**)-1,4-Bis(benzyloxy)-9,10,11,15-tetrahydro-9,10-[3′,4′]furanoanthracene-12,14-diones (8c and 9c).** **8c**/**9c** = 57:43. Purified by column chromatography ($CHCl_3$–hexane–AcOEt, 10:5:1) and recrystallization from $CHCl_3$ to give a mixture of **8c** and **9c** as a white solid (418 mg, 0.86 mmol, 86%), mp 204–206 °C. The diastereoisomers were inseparable by column chromatography and were characterized as a mixture. IR (KBr) 3036, 1867, 1786, 1498, 1267, 1076, 932 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.28 (brs, 2H, 2CHCH(C=O), **9c**), 3.52 (brs, 2H, 2CHCH(C=O), **8c**), 5.00–5.05 (m, 4H, 2OCH_2Ph, **8c** and **9c**), 5.29 (brs, 2H, 2CHCH(C=O), **9c**), 5.42 (brs, 2H, 2CHCH(C=O), **8c**), 6.70 (s, 2H, 2-H, 3-H, **8c**), 6.74 (s, 2H, 2-H, 3-H, **9c**), 7.16–7.20 (m, 2H, 6-H, 7-H, **8c** and **9c**), 7.37–7.50 (m, 12H, 5-H, 8-H, 10PhH, **8c** and **9c**); MS (EI) m/z (relative intensity) 91 (100), 488 (M^+, 26). Anal. Calcd for $C_{32}H_{24}O_5$: C, 78.67; H, 4.95%. Found: C, 78.36; H, 5.30%.

Separation of 8a and 9a with the Difference in Their Solubility in Et_2O. A mixture of **8a** and **9a** (ca. 300 mg) was washed with one portion of Et_2O (ca. 30 mL). The residue was further washed with several portions of Et_2O until **9a** was not observed by ^{1}H NMR spectroscopy. Finally, **8a** was purified by recrystallization from toluene. The first filtrate was evaporated to dryness, and the residue was washed with one portion of Et_2O and then also collected and evaporated. Until the **8a**/**9a** ratio was constant, the washing/evaporation technique was repeated. Finally, recrystallization from toluene produced pure **8a** and **9a**, respectively. Following the above procedure, 10–20 mg of **8a** and **9a** were obtained.

(11*R*,15*S*)-1,4-Dimethoxy-9,10,11,15-tetrahydro-9,10[3′,4′]-furanoanthracene-12,14-diones 8a. Mp 268–270 °C; IR (KBr) 2949, 1778, 1495, 1261, 1078, 928 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.48 (brs, 2H, 2CHCH(C=O)), 3.81 (s, 6H, 2OCH_3), 5.34 (brs, 2H, 2CHCH(C=O)), 6.69 (s, 2H, 2-H, 3-H), 7.18 (dd, J = 3.2, 5.4 Hz, 2H, 6-H, 7-H), 7.41 (dd, J = 3.2, 5.2 Hz, 2H, 5-H, 8-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 38.54, 47.65, 56.38, 110.71, 124.53, 126.92, 127.88, 140.92, 149.12, 170.46; MS (EI) m/z (relative intensity) 223 (94), 238 (100), 336 (M^+, 37). Anal. Calcd for $C_{20}H_{16}O_5$: C, 71.42; H, 4.79%. Found: C, 71.44; H, 5.11%.

(11*S*,15*R*)-1,4-Dimethoxy-9,10,11,15-tetrahydro-9,10[3′,4′]-furanoanthracene-12,14-diones 9a. Mp 252–254 °C; IR (KBr) 2949, 1786, 1499, 1259, 1082, 930 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.47 (brs, 2H, 2CHCH(C=O)), 3.82 (s, 6H, 2OCH_3), 5.30 (brs, 2H, 2CHCH(C=O)), 6.67 (s, 2H, C2,3-H), 7.19 (dd, J = 3.2, 5.4 Hz, 2H, 6-H, 7-H), 7.35 (dd, J = 3.2, 5.2 Hz, 2H, 5-H, 8-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 38.66, 47.46, 55.99, 109.58, 125.31, 127.51, 130.16, 138.37, 148.71, 170.60; MS (EI) m/z (relative intensity) 223 (93), 238 (100), 336 (M^+, 31). Anal. Calcd for $C_{20}H_{16}O_5$: C, 71.42; H, 4.79%. Found: C, 71.46; H, 5.11%.

General Procedure for the Reduction of a Mixture of Cycloadducts 8 and 9. To a suspension of $LiAlH_4$ in dry THF, a solution of a mixture of **8b** and **9b**, or **8c** and **9c** in dry THF were added dropwise at r.t. The mixture was stirred at reflux for 4 h, and then cooled to 0 °C. Water and conc. HCl were then added until the resulting precipitate disappeared. The products were extracted with Et_2O, and the organic phase was washed with brine and dried over Na_2SO_4. Removal of the solvent and drying under vacuum gave a crude mixture of diols **10b** and **11b**, or **10c** and **11c**. The products

were subjected to ^{1}H NMR measurement to determine the **10**/**11** ratio, affording **10b**/**11b** = 43:57 and **10c**/**11c** = 57:43. The products were separated and purified by column chromatography ($CHCl_3$–AcOEt, 2:1).

(11*R*,12*S*)- and (11*S*,12*R*)-9,10-Ethano-11,12-bis(hydroxymethyl)-1,4-dipropoxy-9,10-dihydroanthracenes (10b and 11b). The mixture was obtained in a crude yield of 96%. After multiple column chromatography runs, purified diols **10b** and **11b** were obtained in isolated yields of 33 and 43%, respectively, using the general procedure with $LiAlH_4$ (794 mg, 21.0 mmol) in THF (50 mL) and a mixture of **8b** and **9b** (1.59 g, 4.06 mmol) in dry THF (45 mL). **10b**: a white solid, mp 142–144 °C, R_f = 0.45 ($CHCl_3$–AcOEt, 2:1); IR (KBr) 3275, 2964, 1497, 1259, 1076, 756 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (t, J = 7.3 Hz, 6H, $2CH_2CH_3$), 1.78–1.85 (m, 4H, $2CH_2CH_2CH_3$), 2.33–2.35 (m, 2H, $2CHCHCH_2OH$), 2.58 (brs, 2H, $2CH_2OH$), 3.35–3.42 (m, 4H, $2CHCH_2OH$), 3.84–3.93 (m, 4H, $2OCH_2CH_2$), 4.75 (brs, 2H, $2CHCHCH_2OH$), 6.58 (s, 2H, 2-H, 3-H), 7.12 (dd, J = 3.2, 5.4 Hz, 2H, 6-H, 7-H), 7.31 (dd, J = 3.2, 5.2 Hz, 2H, 5-H, 8-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.72, 22.78, 40.47, 43.51, 63.70, 70.60, 109.79, 123.50, 125.67, 130.75, 143.45, 148.93; MS (EI) m/z (relative intensity) 294 (100), 382 (M^+, 35). Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91%. Found: C, 75.36; H, 8.09%. **11b**: a white solid, mp 155–157 °C, R_f = 0.38 ($CHCl_3$–AcOEt, 2:1); IR (KBr) 3327, 2966, 1495, 1257, 1070, 1011 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (t, J = 7.3 Hz, 6H, $2CH_2CH_3$), 1.78–1.85 (m, 4H, $2CH_2CH_2CH_3$), 2.34–2.36 (m, 2H, $2CHCHCH_2OH$), 2.72 (brs, 2H, $2CH_2OH$), 3.28 (dd, J = 9.6, 11.6 Hz, 2H, $2CHCH_AH_BOH$), 3.65 (dd, J = 2.9, 11.6 Hz, 2H, $2CHCH_AH_BOH$), 3.82–3.94 (m, 4H, $2OCH_2CH_2$), 4.63 (brs, 2H, $2CHCHCH_2OH$), 6.58 (s, 2H, 2-H, 3-H), 7.08 (dd, J = 3.2, 5.4 Hz, 2H, 6-H, 7-H), 7.23 (dd, J = 3.2, 5.2 Hz, 2H, 5-H, 8-H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.67, 22.76, 41.15, 42.95, 64.99, 71.30, 110.51, 124.69, 125.66, 133.54, 141.16, 147.76; MS (EI) m/z (relative intensity) 294 (100), 392 (M^+, 32). Anal. Calcd for $C_{24}H_{30}O_4$: C, 75.36; H, 7.91%. Found: C, 75.07; H, 7.82%.

(11*R*,12*S*)- and (11*S*,12*R*)-1,4-Bis(benzyloxy)-9,10-ethano-11,12-bis(hydroxymethyl)-9,10-dihydroanthracenes (10c and 11c). The mixture was obtained in a crude yield of 91%. After multiple column chromatography runs, purified diols **10c** and **11c** were obtained in isolated yields of 36 and 28%, respectively, using the general procedure with $LiAlH_4$ (133 mg, 3.50 mmol) in THF (10 mL) and a mixture of **8c** and **9c** (379 mg, 0.78 mmol) in dry THF (15 mL). **10c**: a white solid, mp 203–205 °C, R_f = 0.42 ($CHCl_3$–AcOEt, 2:1); IR (KBr) 3265, 2961, 1499, 1263, 1034, 752 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.33–2.36 (m, 2H, $2CHCHCH_2OH$), 2.51 (brs, 2H, $2CH_2OH$), 3.39 (dd, J = 7.7, 11.2 Hz, 2H, $2CHCH_AH_BOH$), 3.47 (dd, J = 5.4, 11.2 Hz, 2H, $2CHCH_AH_BOH$), 4.80 (brs, 2H, $2CHCHCH_2OH$), 5.00–5.06 (m, 4H, $2OCH_2Ph$), 6.65 (s, 2H, 2-H, 3-H), 7.12 (dd, J = 3.2, 5.4 Hz, 2H, 6-H, 7-H), 7.31 (dd, J = 3.2, 5.2 Hz, 2H, 5-H, 8-H), 7.35–7.45 (m, 10H, 10PhH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 40.50, 43.60, 63.70, 71.02, 110.16, 123.61, 125.78, 127.31, 127.93, 128.63, 131.19, 137.36, 143.26, 148.98; MS (EI) m/z (relative intensity) 91 (100), 478 (M^+, 28). Anal. Calcd for $C_{32}H_{30}O_4$: C, 80.31; H, 6.32%. Found: C, 80.35; H, 6.61%. **11c**: a white solid, mp 75–77 °C, R_f = 0.32 ($CHCl_3$–AcOEt, 2:1); IR (KBr) 3385, 2930, 1493, 1259, 1042, 741 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.25–2.27 (m, 2H, $2CHCHCH_2OH$), 2.78 (brs, 2H, $2CH_2OH$), 3.24 (dd, J = 9.6, 11.2 Hz, 2H, $2CHCH_AH_BOH$), 3.61 (dd, J = 2.9, 11.2 Hz, 2H, $2CHCH_AH_BOH$), 4.66 (brs, 2H, $2CHCHCH_2OH$), 5.01–5.06 (m, 4H, $2OCH_2Ph$), 6.65 (s, 2H, 2-H, 3-H), 7.09 (dd, J = 3.2, 5.4 Hz, 2H, 6-H, 7-H), 7.23 (dd, J = 3.2, 5.2 Hz, 2H, 5-H, 8-H), 7.34–7.44 (m, 10H, 10PhH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 41.25, 42.84, 64.86, 71.48, 111.00, 124.75, 125.72, 127.48, 127.87, 128.55, 133.89, 137.49, 140.93, 148.74; MS (EI) m/z (relative intensity) 91 (100), 478 (M^+, 26). Anal. Calcd for $C_{32}H_{30}O_4$: C, 80.31; H, 6.32%. Found: C, 80.02; H, 6.25%.

Crystal Structure Determinations. X-ray data were collected on a Rigaku/MSC MERCURY CCD. The structures were solved by direct methods[17] and expanded using the Fourier technique.[18] All calculations were performed using the teXsan program packages.[19] Full crystallographic details, excluding structure factors, for the structures of compounds **8a** (CCDC 207475), **9a** (CCDC 207474), and **10b** (CCDC 212776) have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.ca.ac.uk].

Crystal Data for 8a. $C_{20}H_{16}O_5$, M = 336.34, triclinic, space group $P\bar{1}$ (#2), a = 7.834(6), b = 9.496(7), c = 11.694(9) Å, α = 105.507(7), β = 98.392(7), γ = 105.044°, V = 787(1) Å^3, Z = 2, D_{calcd} = 1.418 g cm^{-3}, μ(Mo Kα) = 1.02 cm^{-1}, T = 223 K; 29480 reflections collected, 3155 unique with $I > 2\sigma(I)$ (R_{int} = 0.018), R = 0.051, R_w = 0.079.

Crystal Data for 9a. 2($C_{20}H_{16}O_5$)·0.5toluene, $C_{43.5}H_{36}O_{10}$, M = 778.96, triclinic, space group $P\bar{1}$ (#2), a = 11.208(6), b = 11.681(6), c = 13.466(7) Å, α = 90.137(6), β = 101.857(7), γ = 94.414(5)°, V = 1719(1) Å^3, Z = 4, D_{calcd} = 1.219 g cm^{-3}, μ(Mo Kα) = 1.05 cm^{-1}, T = 223 K; 69320 reflections collected, 7707 unique with $I > 2\sigma(I)$ (R_{int} = 0.029), R = 0.063, R_w = 0.084.

Crystal Data for 10b. $C_{24}H_{30}O_4$, M = 382.50, triclinic, space group $P\bar{1}$ (#2), a = 9.716(2), b = 10.742(2), c = 11.137(1) Å, α = 73.02(1), β = 70.40(1), γ = 87.85(2)°, V = 1045.1(4) Å^3, Z = 2, D_{calcd} = 1.215 g cm^{-3}, μ(Mo Kα) = 0.81 cm^{-1}, T = 296 K; 11616 reflections collected, 4638 unique with $I > 2\sigma(I)$ (R_{int} = 0.076), R = 0.096, R_w = 0.114.

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