Distortion of Olefin and Carbonyl π-Orbitals in Dibenzobicyclo[2.2.2]octatrienes and Dibenzobicyclo[2.2.2]octadienones. Unsymmetrization of π Lobes Arising from π–π Orbital Interactions

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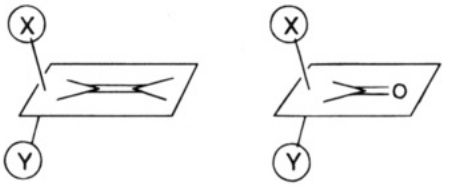
We have detected the unsymmetrical π faces of the olefin group in 2-substituted dibenzobicyclo-[2.2.2]octatrienes (2-substituted 9,10-dihydro-9,10-ethenoanthracenes) and the carbonyl groups of 2-substituted and 3-substituted dibenzobicyclo[2.2.2]octadienones (2-substituted and 3-substituted 9,10-dihydro-9,10-(11-ketoethano)anthracenes), wherein σ-type overlaps of the π orbitals are involved, in a similar manner to longicyclic conjugation. An intrinsically nonequivalent substituent at distal positions modulates the epoxidation and dihydroxylation of the olefin group and the reduction of the carbonyl group. Both systems exhibit similar substituent effects: an "electron-withdrawing" substituent such as a nitro or fluoro group gave a large to moderate bias (preferred *syn* attack with respect to the substituent) whereas an "electron-donating" methoxy substituent exhibited a negligible bias. Herein we interpret these biases or nonbiases in terms of unsymmetrization of π lobes of the olefin and carbonyl π orbitals, arising from nonequivalent π–π interactions rather than from an electron-donating or -withdrawing effect.

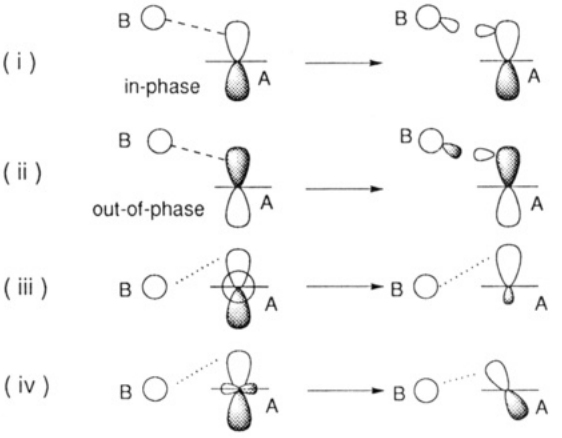
π Orbitals of trigonal carbon atoms of an olefin or a carbonyl group have a symmetric property, i.e., they are symmetric in magnitude and antisymmetric in sign. This nodal property constitutes a symmetric π face (π plane) of olefin and carbonyl groups. However, some olefinic and carbonyl compounds afford a biased pair of reaction products even when the stereogenic center is free from steric bias.[1] These observations can be interpreted in terms of involvement of an unsymmetrical π face of these reactive π centers. Substituents asymmetric with respect to the π plane can destroy the symmetric magnitudes of the π orbital lobes (Chart 1 and Scheme 1).

Phenomenologically, the effects of substituents (in particular, those free from significant steric interference) on the π centers of olefin and carbonyl groups can be classified as follows (Table 1): equivalent substituents on both sides essentially do not perturb π face symmetry, regardless of whether interaction is present (case a) or absent (case b). Nonequivalent substituents do perturb the π face and will produce a biased pair of products (case c). This is not always the case, however. Even in the presence of the interaction of nonequivalent substituents, the π face can still be equivalent when the interaction is symmetric or cancelled (case d). When the interaction between the nonequivalent substituents and the π center is absent, of course, there is no perturbation of the π face (case e), which corresponds to orbital non-interaction, owing to symmetry disagreement.[2] Precisely speaking, case d can be regarded as an extremely weak asymmetric interaction of nonequivalent substituents, which is, in fact, different from noninteraction (case e). Defining these three cases (c–e) is of theoretical importance because *chemical intuition will not distinguish them*. In a recent publication we proposed unsymmetrization of π orbitals of olefin and carbonyl groups through nonequivalent orbital interactions on each lobe of the π orbitals.[3,4]

Chart 1



Scheme 1. Orbital Distortions[a]



[a] Primary orbital interactions between fragments A and B (i and ii) and secondary orbital interactions in fragment A (iii and iv).

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1994.

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Table 1. Perturbations of π Face of Olefin and Carbonyl Groups

case	substituent	interaction	π face	reaction product
a	X = Y	equivalent	symmetric	50:50
b	X = Y	absent	symmetric	50:50
c	X ≠ Y	nonequivalent	asymmetric	biased
d	X ≠ Y	equivalent[a]	symmetric	50:50
e	X ≠ Y	absent	symmetric	50:50

[a] Precisely speaking, "nonequivalent interaction" is small or negligible.

We analyzed orbital distortions of these π orbitals in terms of perturbation theory:[5] molecular orbitals of the whole molecule are considered to be constructed from orbitals of the composite subsystems, the olefin (or carbonyl) moiety, and the remaining framework. We have postulated that the first-order interactions of these fragment orbitals can unsymmetrize the π lobes of the olefin or carbonyl π orbitals (Scheme 1i,ii).[3] These first-order interactions involve two possible combinations, in-phase and out-of-phase combinations of the interacting orbitals,[6] although these mixings will not by themselves create a second-order hybridization (Scheme 1iii) or tilting (Scheme 1iv) of the π and π^* orbitals to one face of the π bond.[7] Second-order orbital interactions involve mixing together of the orbitals of a molecule or the atomic orbitals of an individual atom (for example, on atom A in Scheme 1iii,iv), intrinsically orthogonal, through the interaction of an intervening orbital B. Some theories emphasize these resultant changes of the shape of orbitals derived from the second-order mixing, in order to interpret the unsymmetrical π face.[7] These distortions may stem from secondary orbital interactions.[8] In this paper we will describe detection of the unsymmetrical π face of the olefin groups in 2-substituted dibenzobicyclo-[2.2.2]octatrienes (2-substituted 9,10-dihydro-9,10-ethenoanthracenes) **1** and the carbonyl groups of 2-substituted (**2**) and 3-substituted dibenzobicyclo[2.2.2]-octadienones (**3**) (2- and 3-substituted 9,10-dihydro-9,-10-(11-ketoethano)anthracenes), wherein σ-type overlaps of the π orbitals are involved, in a manner similar to longicyclic conjugation.[9,10] An intrinsically nonequivalent substituent at distal positions modulates the direction of electrophilic epoxidation and dihydroxylation of the olefin group and the nucleophilic reduction of the carbonyl group. Both systems exhibited a similar substituent effect: an "electron-withdrawing" substituent such as a nitro or a fluoro group gave a large to moderate bias (preferred *syn* attack with respect to the substituents) whereas an "electron-donating" methoxy substituent exhibited a small or negligible bias. These observations afford experimental examples of the situations designated as cases c–e in Table 1 (*vide post*). Herein we interpret these biases in terms of orbital perturbation arising from the first-order π–π interactions rather than electron-donating or -withdrawing character.

Preparation of Dibenzobicyclo[2.2.2]octane Derivatives. Bicyclic structures of target molecules were constructed by the Diels–Alder cyclization of anthracene and an appropriate dienophile, followed by introduction of substituents through aromatic nitration. The parent dibenzobicyclo[2.2.2]octatriene (**1a**) was prepared as previously described, i.e., through the decarbonylation of 11,12-dicarboxydibenzobicyclo[2.2.2]octatriene (Figure 1).[11] Because conventional nitration of the parent hydrocarbon **1a** is accompanied with side reactions (nitration of the olefin moiety), 2-nitrodibenzobicyclo[2.2.2]octatriene (**1b**) was prepared through nitration of the precursor diester, 11,12-dimethylcarboxydibenzobicyclo[2.2.2]octatriene, the adduct of anthracene and dimethyl acetylenedicarboxylate, followed by hydrolysis and decarbonylation. 2-Methoxydibenzobicylo[2.2.2]octatriene (**1c**) was prepared from the 2-amino derivative, obtained by reduction of the 2-nitro derivative **1b** over iron in the presence of aqueous hydrogen chloride, followed by diazotization, hydroxy-dediazoniation, and methylation. The 2-fluoro derivative **1d** was obtained from 2-fluoroanthracene in a manner similar to that described for **1a**.[12]

The parent dibenzobicyclo[2.2.2]octadienone **2a** (= **3a**) was prepared as previously described with some modification (Figure 1) (see Experimental Section).[13] Nitration of the parent ketone **2a** with acetyl nitrate yielded a mixture of the nitro ketone (2- (**2b**) and 3-nitro isomers (**3b**)) in a ratio of 1:1. These nitro ketones were converted into methoxy and fluoro derivatives: 2- and 3-methoxydibenzobicyclo[2.2.2]octadienones (**2c** and **3c**) were prepared from the amino derivatives (obtained by hydrogenation of **2b** and **3b**, respectively), followed by diazotization, hydroxy-dediazoniation, and methylation; 2- and 3-fluorodibenzobicyclo[2.2.2]octadienones (**2d** and **3d**) were prepared from the corresponding amino compounds, followed by the Siemann reaction with hydrogen tetrafluoroborate as a source of the fluorine atom.[14]

Electrophilic Oxidative Reactions of the Olefins. Epoxidation and dihydroxylation of the olefin moiety of 2-substituted dibenzobicyclo[2.2.2]octatrienes **1a–d** were investigated (Figure 2). 2-Nitrodibenzobicyclo[2.2.2]-octatriene (**1b**) undergoes preferential *syn*-addition (with respect to the nitro group) of peroxidic reagents, i.e., *m*-chloroperbenzoic acid, osmium tetraoxide, and potassium permanganate. The results are summarized in Table 2, together with those for the parent **1a**. In the epoxidation of **1b** with *m*-CPBA, the *syn* epoxide **4b-*syn*** is favored over the *anti* epoxide **4b-*anti***. In the dihydroxylation with osmium tetraoxide[15] or potassium permanganate,[16] the *syn* diol **5b-*syn*** is also favored over the

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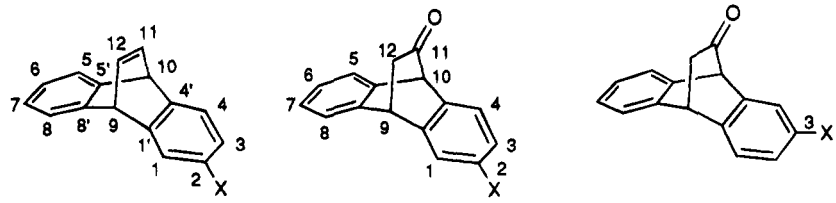

1a: X = H
1b: X = NO_2
1c: X = OCH_3
1d: X = F

2a: X = H
2b: X = NO_2
2c: X = OCH_3
2d: X = F

3a: X = H
3b: X = NO_2
3c: X = OCH_3
3d: X = F

Figure 1.

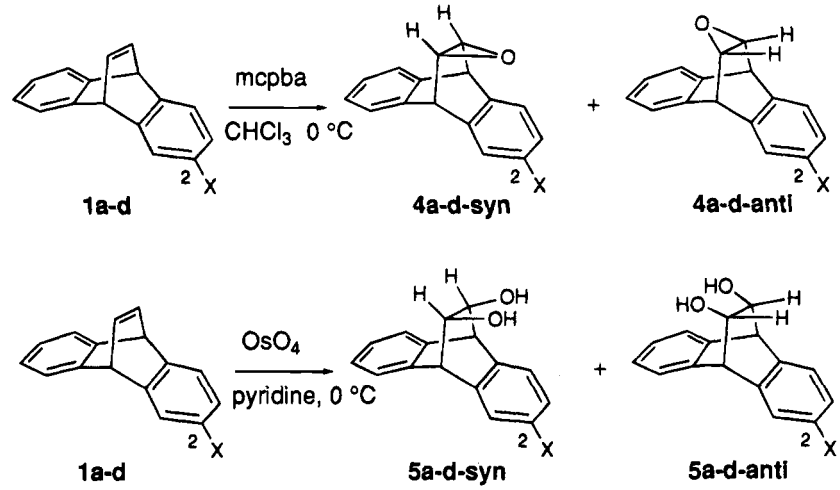

Figure 2.

Table 2. Isomer Distributions in the Attack of Electrophilic Oxidative Reagents on 2-Substituted Dibenzobicyclo[2.2.2]octatrienes

	substituent X	reagent	condns (°C, h)	yield (%)	*syn*:*anti*
1a	H	*m*-CPBA	0, 41	88[a]	50:50
1a	H	OsO_4	−27, 5	90	50:50
1a	H	$KMnO_4$	−14, 0.5	58	50:50
1b	NO_2	*m*-CPBA	0, 48	46[b-d]	77:23
1b	NO_2	OsO_4	−27, 3	67	85:15
1b	NO_2	$KMnO_4$	−14, 0.5	48	88:12
1c	OCH_3	*m*-CPBA	0, 42	63	48:52
1c	OCH_3	OsO_4	−27, 1.5	96	48:52
1d	F	*m*-CPBA	0, 32	86	58:42
1d	F	OsO_4	−23, 2.5	96	68:32

[a] 20 °C, 2 h: 83% yield. [b] 43% recovery. [c] 20 °C, 48 h: 89% (*syn*:*anti* = 76:24). [d] 0 °C, 212 h: 77% (*syn*:*anti* = 73:27) and recovery (8%).

anti diol **5b-*anti***. The epoxidation with *m*-CPBA at high reaction temperature (20 °C) did not significantly alter the ratio of syn to anti isomers (see Table 2). Values of diastereomeric excess observed in these reactions ranged from 54% to 76%. Direct participation of the oxygen atoms of the nitro group at the reaction center, such as a coordinative interaction, cannot account for these results, judging from the distance (at least 6 Å) from the ethylenic carbon atom. 2-Fluorodibenzobicyclo[2.2.2]-octatriene (**1d**) also preferentially gave the *syn* epoxide (**4d-*syn***) and the *syn* diol (**5d-*syn***). On the other hand, the 2-methoxy substrate **1c** showed a negligible preference in the reactions, giving a slight excess of the *anti* products (**4c-*anti*** and **5c-*anti***).

The configurations of the epoxide moieties of **1b** (**4b**), **1c** (**4c**), and **1d** (**4d**) were elucidated on the basis of the characteristic deshielding of the H-5 and H-8 protons (in the case of the *syn* epoxides) or H-1 and H-4 protons (in the case of the *anti* epoxides) owing to the anisotropic effect of the epoxide ring. The configuration of the major isomer of the epoxide of **1b** (**4b-*syn***) was also confirmed by X-ray crystallographic analysis. A similar shielding effect of an epoxide ring on benzobicyclo[2.2.2]octenes has been discussed previously,[17] supporting the assignments. The diols **5b-*syn*** and **5d-*syn*** can be converted to the dimethyl acetals, confirming the *cis* relationship of the two hydroxy groups. The mixture of diols of the methoxy compound **5c** was separated after the formation of dimethyl acetals. NOE enhancements between the acetal methyl protons (of the more shielded methyl group) and the aromatic protons (H_1−H_4) also supports the configurations. Furthermore, the lack of perturbation of the aromatic protons opposite the diols upon acetal formation is also in accord with the above assignments.

Simple considerations based on the π-electron density of the two benzo moieties would lead us to a contradictory interpretation:[18,19] an electron-withdrawing (e.g., nitro) substituent would favor the *anti* addition of electrophilic oxidative reagents, and *syn* addition would be favored in the case of an electron-donating (e.g., methoxy) substituent because electron donation from an electron-rich aromatic ring to the π_{CC} orbital accumulates electron

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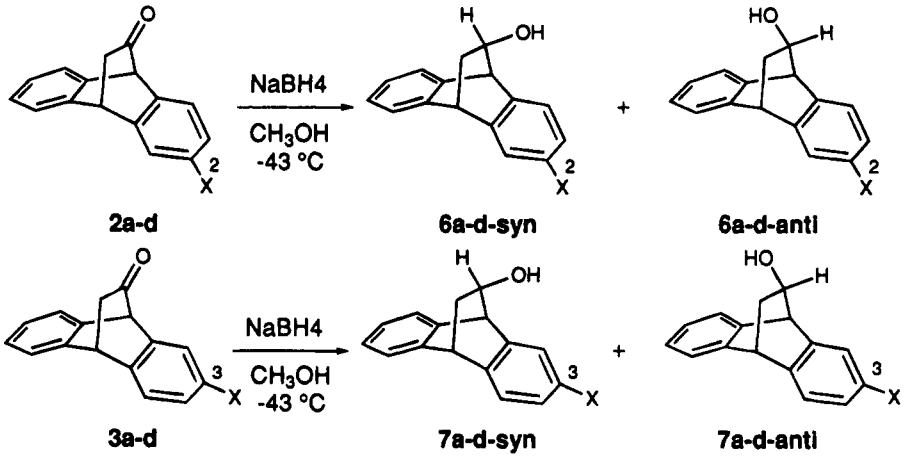

Figure 3.

density on the side opposite the nitro group or on the same side as the methoxy group. The results of the reactions of the olefins are, however, in conflict with these ideas. Furthermore, judging from the strong π electron-donating ability of a methoxy group,[18,19] a large bias would be expected in the reaction of the methoxy compound **1c**. However, this is not the experimental outcome. On the other hand, Cieplak's postulation[20] suggests ability of the exocyclic phenyl σ bonds ($C_{4'}$–C_{10} and $C_{1'}$–C_9 bonds of **1b–d** in Figure 1) to function as a donor to the vacant incipient $\sigma^{*\ddagger}$ orbital. As shown in our previous aromatic systems, spiro[cyclopentane-1,9'-fluorene] systems, a methoxy substituent induced a moderate bias.[3] Therefore, inductive electron-withdrawing ability and resonance electron-donating ability of a methoxy group at the distal position seems to superficially balance in the present system (**1c**).

(19) The substituents NO_2, OCH_3, and F will certainly change the electrostatic potential considerably, and thus a dipolar or charged particle will be influenced. The PM3-based electrostatic potential fields indicated the substituent effect on the π face of the olefins **1a–1d** (electrostatic potential fields (EPF), see: Scrocco, E.; Tomasi, J. *Fortschr. Chem. Forsth.* **1973**, *42*, 95–170). NO_2 group: a positive EPF distribution with a depth (2.5–5.0 kcal/mol) is found near the double bond on the side of the nitrobenzene moiety in **1b**, as the strong electron-withdrawing nitro substituent creates a significant electron deficiency at the carbon atoms of the nitrobenzene ring. Such a positive EPF region is in accordance with the classical description which involves electron delocalization of the aromatic π electrons to the nitro group. On the other hand, a negative EPF distribution with a depth of −10 kcal/mol, assigning to π electrons of the unsubstituted benzene, is placed above and below the benzene-ring plane of **1b** which may facilitate the anti-attack of a highly polar or positively charged electrophilic reagent. However, this is not experimental reality in the case of the reactions with *m*-CPBA and osmium tetraoxide. Interaction of the positive EPF region with lone-pair electrons of the attacking reagent, or stabilization of a possible highly polar transition state (such as a peroxirane, see: Paquette, L. A.; Bellamy, F.; Bellamy, G. J.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1981**, *103*, 7122–7133) by the positive EPF region can partially contribute to the syn attack observed in **1b**. OH (or CH_3O) group: a strong negative EPF region with a depth (−20 kcal/mol) was found in the space surrounding the oxygen atom of **1c** (a hydroxy group was used for the sake of simplicity in calculations) which could be attributed to two lone pairs of the oxygen atom, although such a negative region was attenuated gradually apart from the oxygen atom. On the other hand a positive EPF region is not significantly extended on both sides of the olefinic moiety. Therefore, judging from the negative EPF distribution syn attack of a highly polar or positively charged electrophilic agent might be favored. F group: although a significant positive EPF distribution is not found on both sides of the olefin moiety of **1d**, a negative EPF region is found on the side of the unsubstituted benzene moiety whereas a negative EPF region became contracted above and below the fluorobenzene ring plane owing to an electron-accepting fluoro substituent. Anti-attack of a highly polar or positively charged electrophilic reagent might be expected in terms of the EPF representations.

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Table 3. Isomer Distributions in Alcohols Formed by Reduction of 2- and 3-Substituted Dibenzobicyclo[2.2.2]octadienones at −43 °C

	substituent X	time (h)	yield (%)	*anti*:*syn*
2a	H	2	93	50:50
2b	NO_2	2	64[a]	77:23
2c	OCH_3	1	99	46:54
2d	F	1	95	57:43
3b	NO_2	1.5	80	77:23
3c	OCH_3	1.5	98	49:51
3d	F	1	94	61:39

[a] Recovery (18%).

Reduction of the Ketones. Reduction of the carbonyl moiety of 2- (**2**) and 3-substituted dibenzobicyclo[2.2.2]octadienones (**3**) was investigated (Figure 3, Table 3). Substituent effects were found to be similar in both 2- and 3-substituted ketones, although the distance between the reaction center and the substituent is remote and different in direction. The 2- (**2b**) and 3-nitrodibenzobicyclo[2.2.2]octadienones (**3b**) preferentially gave *anti* alcohols (**6b-*anti*** and **7b-*anti***) on reduction with hydride ion, i.e., *syn* attack, with values of diastereomeric excess of 54% and 54%, respectively. A fluoro substituent (in **2d** and **3d**) also favors *syn* addition to give an *anti* alcohol. On the other hand, a methoxy group (in **2c** and **3c**) modifies the preference in the reduction reaction, giving a negligible bias with a slight excess of the *syn* product in the case of **2c**.

The configurations of the *anti*-alcohols were elucidated on the basis of the characteristic low-field shifts of the H5 or H8 proton of the unsubstituted benzene moiety.[21] The configurations of the minor isomer of the alcohol of **2b** (**6b-*syn***) and of the major isomer of the alcohol of **3b** (**7b-*anti***) were also confirmed by X-ray crystallographic analysis.

Although electron delocalization theory[18,22] can interpret the experimental bias of the reduction, it is unable to rationalize the small extent of the bias in the case of the methoxy substituent (**2c** and **3c**), judging from the strong π-donating ability. We have pointed out the divergent substituent effect of a methoxy group in the previous aromatic systems, spiro[cyclopentane-1,9'-fluorene] systems,[3] where the methoxy group effected the bias.

Orbital Interaction Principles. In order to interpret the experimental bias in the reactions of the olefin

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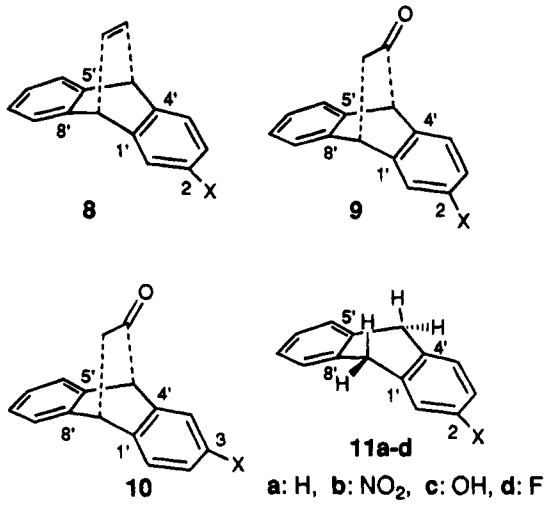


Figure 4.

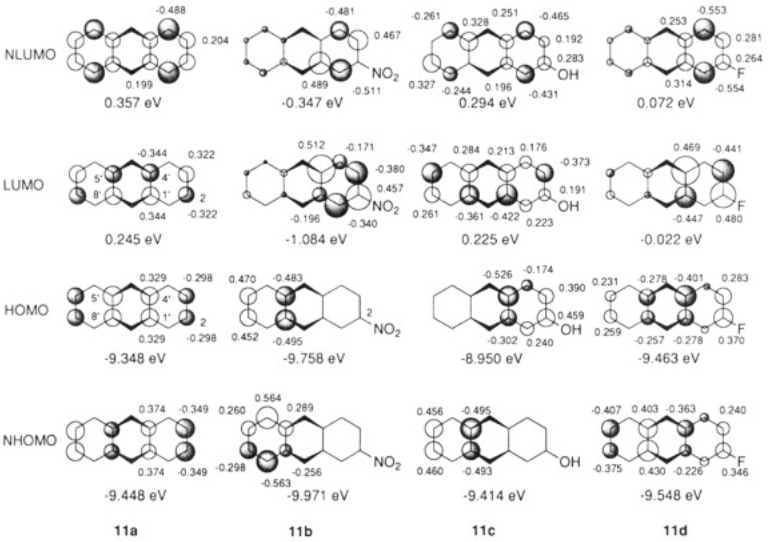
1 and the ketones **2** and **3** in a unified manner, we considered the orbital distortion effects on the reactive π orbitals on the basis of the perturbation theory.[5] The reactions of the olefin and the carbonyl group involve different π orbitals, i.e., the occupied π orbital of the olefin (π_{CC}) and the vacant π orbital of the ketone (π^*_{CO}). To reveal the perturbation at the π reaction center (π_{CO} and π^*_{CO}) arising from the first-order interactions of the aromatic π orbitals, orbitals of the olefinic or carbonyl molecules are considered to be constructed from orbitals of the composite subsystems, a convex dihydroanthracene (**11a–d**) and an olefin group or a carbonyl group (**8–10**, Figure 4) (*vide post*). In these combinations, π orbitals of the aromatic moieties and that of the olefin group or of the carbonyl group can interact predominantly through the *ipso* (C-1′, C-4′, C-5′, and C-8′) positions, involving σ-type overlaps of these π orbitals.[7b] Our orbital interaction motif for unsymmetrization of the π orbitals is based on simple, well-defined principles of orbital interactions, as follows. Principle 1: in-phase mixing of orbitals (of fragments A and B, for example) leads to buildup of bonding electrons along the internuclear region (of a combined molecule A–B), and out-of-phase mixing of orbitals (A and B) depletes the bonding electrons from the internuclear region (A–B).[6] In order to emphasize electron density distribution of the internuclear region in addition to the phase relation of the interacting orbitals, we adopted the diagram depicted in Scheme 1a,b: the buildup of bonding electron is equivalent to diffusion of the electron into each bonding region along the bond axis (Scheme 1i); the removal of bonding electron from the internuclear region can be regarded as diffusion of the electron of each fragment into each antibonding region along the internuclear axis (Scheme 1ii).[3] In the case of orbital interactions of two vacant orbitals, the depletion and buildup of the orbital electron density (or the diffusion of orbital into the internuclear region) are notional because there is no electron present. However, we are interested in the interpretation of the reaction in terms of frontier orbital theory.[5] We thus consider the virtual electron density (and virtual orbital diffusion region) which is to be attacked by electrons of an occupied orbital (e.g., the HOMO) of a reagent.[3] The bonding or antibonding diffusion depends on energy difference and on overlap: interactions of orbitals with a smaller energy gap or with a larger set of overlap integrals more significantly perturb the electron density distribution in the interacting region. Principle 2: out-of-phase combination of HOMO (fragment A) and HOMO (fragment B), if symmetry permits, results in a hybridized HOMO (A–B), activated energetically, while in-phase combination of LUMO (fragment A) and LUMO (fragment B), if symmetry permits, results in a hybridized LUMO of A–B, activated energetically.[5a,6,23] These principles can also describe orbital distortions in π–π interactions in spiro[cyclopentane-1,9′-fluorene] systems[3] and in dihedral-angle-dependent σ–π interactions in norbornene and norbornanone.[4]

Orbital Interaction Motifs in the Electrophilic Oxidations of the Olefins. Symmetry in these reactions allows the interaction of a vacant MO of the peracid, the permanganate ion, or osmium tetraoxide with the occupied MO of the ethylenic π bond (the HOMO).[15,16,24] In order to reveal the perturbation of the π orbital of the ethylene arising from the nonequivalent substituents in the substituted dibenzobicyclo[2.2.2]octatrienes **1**, the molecules are assumed to be constructed from the orbitals of the convex-substituted dihydroanthracene **11a–d** and the ethylene **8** (Figure 4).[7b] The π orbitals of the dihydroanthracene can also be further analyzed as a combination of π orbitals of the two benzene moieties. Convex dihydroanthracenes such as dihydroanthracene (**11a**), 2-nitrodihydroanthracene (**11b**), 2-hydroxydihydroanthracene (**11c**) (used in place of 2-methoxydihydroanthracene for the sake of simplicity in calculations), and 2-fluorodihydroanthracene (**11d**) were calculated by applying semiempirical PM3 methods,[25] and coefficients of frontier orbitals and their vicinities are shown in Chart 2. The HOMO of the unsubstituted dihydroanthracene (**11a**) in convex geometry is essentially derived from the in-phase combination of the HOMO's of the two benzene nuclei. The level ordering was modified by the through-bond coupling of the two aromatic π orbitals through the pseudo π orbital (π_{CH_2}) of the insulating methylene group:[26] the in-phase combination of the HOMO's of the two aromatic rings is higher in energy than the out-of-phase combination (although the energy difference is small, 2.3 kcal/mol, by PM3). The symmetric HOMO (PM3; −9.348 eV) of **11a** cannot interact with the antisymmetric π orbital of the ethylene; alternatively, the NXHOMO (PM3: −9.448 eV) interacts with the π_{CC} of the ethylene in an out-of-phase combination,[7b] although this symmetric interaction leads to no unsymmetrization of the lobes of the π_{CC} of the ethylene. This motif corresponds to case a defined in Table 1.

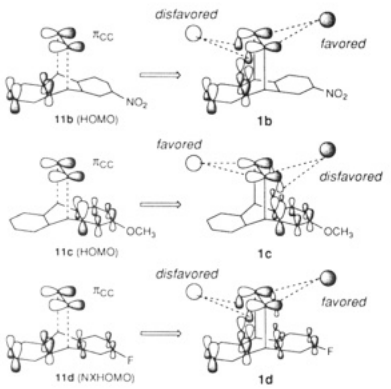
(22) A similar substituent effect on the PM3-based electrostatic potential fields was found in the π face of the ketones **2(3)a–d** as in the case of the olefins (see ref 19). NO_2 group: syn attack of a highly polar or negatively charged nucleophile will be facilitated by the interaction of the positive EPF region on the side of the nitrobenzene moiety of **2b**. This situation is in accordance with the description of the simple electron density theory. This attractive electrostatic interaction can make a partial contribution to the observed syn addition. OH (CH3O) group: syn attack of a highly polar or negatively charged nucleophilic reagent might be facilitated due to a strong negative EPF distribution of the oxygen atom of **2c** and **3c**. F group: anti-attack of a highly polar or negatively charged nucleophilic agent might be disfavored due to the negative EPF distribution on the side of the fluorobenzene moiety of **2d**.

(23) Klein, J. *Tetrahedron Lett.* **1973**, 4307–4310. Klein, J. *Tetrahedron* **1974**, *30*, 3349–3353.
(24) Fukui, K. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 498–507.
(25) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209–221.
(26) Hoffmann R. *Acc. Chem. Res.* **1971**, *4*, 1–9. Heilbroner, E.; Schmelzer, A. *Helv. Chim. Acta* **1975**, *58*, 936–967. See also ref 7b.

Chart 2. Frontier Orbitals and Their Vicinities of Substituted Dihydroanthracenes in Convex Geometry



Scheme 2. Distortion of the Olefinic π Orbital



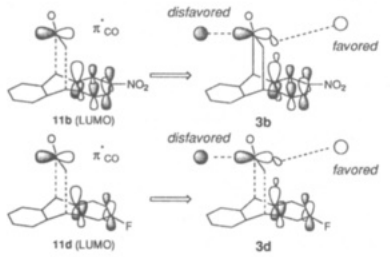
A substituent destroys the symmetrical arrangements of the HOMO and the NXHOMO of the dihydroanthracene. The HOMO's of substituted dihydroanthracenes **11b**−**d** in convex geometry are energetically higher-lying than that of the ethylene (π_{CC}, HOMO, −10.640 eV, PM3). The lower-lying HOMO of the ethylene can mix with the HOMO of **11b**−**d** in an out-of-phase fashion to give the energetically activated hybridized HOMO of the whole molecules, which will determine the direction of the attack of the vacant orbital of the oxidative reagent. The HOMO (PM3: −9.758 eV) of 2-nitrodihydroanthracene (**11b**) is essentially localized on the unsubstituted benzene moiety, stemming predominantly from the HOMO (PM3: −9.751 eV; degenerate) of the benzene, which is higher in energy than the HOMO (PM3: −10.602 and −10.847 eV; almost degenerate) of the nitrobenzene (Chart 2). The orbital phase agreement favors the interaction of the ethylene (HOMO) with the HOMO (PM3: - 9.758 eV) of 2-nitrodihydroanthracene (**11b**). The out-of-phase overlap of these π orbitals raises the energy of the olefin moiety, involving the depletion of the electron density in the internuclear region, i.e., antibonding orbital diffusion (Scheme 2).[3] Therefore, the electrophilic oxidative reagents attack the olefinic π lobe opposite the depleted region, that is, from the same side as the substituent. This motif corresponds to case c in Table 1.

In the case of an electron-donating hydroxy group, an out-of-phase combination of π_{CC} of the olefin with the HOMO of 2-hydroxydihydroanthracene (**11c**) raises the energy so as to activate the π_{CC} fragment to the attack of an electrophile. The HOMO (PM3: −8.950 eV) of 2-hydroxydihydroanthracene (**11c**) also has biased orbital amplitudes localizing on the phenol moiety, not on the benzene moiety, because of the higher level of the HOMO of phenol (PM3: −9.174 eV) than that of benzene (PM3: −9.751 eV) (Chart 2). A larger overlap results in greater amplitudes of the antibonding region between nuclei. The depleted region, arising from the orbitals on the phenol moiety, disfavors the attack of the electrophile (Scheme 2). Therefore, the π_{CC} fragment intrinsically favors the attack of an electrophile on the side opposite the hydroxy group. However, the HOMO of **11c** increases the energy separation from the HOMO of ethylene (−9.758 eV, PM3) by 13.63 kcal/mol as compared with the case of the nitro substituent **1b** (Chart 2). The large energy gap of these interactive fragments would decrease the effect significantly. Thus, the reactions of 2-methoxydibenzobicyclo[2.2.2]octatriene (**1c**) with *m*-CPBA and osmium tetraoxide showed a slight distortion of the π face of the olefin moiety (Table 2). This interaction diagram can be regarded as case d, designated in Table 1.

A fluorine atom is also an electron-withdrawing substituent which can be discussed analogously with the nitro substituent. The HOMO (−9.463 eV, PM3) of 2-fluorodihydroanthracene (**11d**) is constructed from the in-phase combination of the fluorobenzene and the benzene moieties (Chart 2).[27] Instead, symmetry encourages mixing of π_{CC} of the ethylene with the lower-lying NXHOMO (−9.548 eV) of **11d** in an out-of-phase manner. At the points of interaction (at C-1′/C-4′ and C-5′/C-8′), different amplitudes of the wave functions of the NXHOMO (**11d**) result in different buildup of the antibonding region between nuclei (Scheme 2). A larger depleted region greatly reduces the electron-donating ability toward the attack of the electron-deficient orbital of an electrophile. Thus, the π_{CC} orbital favors the attack of the reagent on the side of the substituent, providing a rational interpretation of the observed bias.

(27) The amplitudes at the *ipso* positions (C_1/$C_{4'}$ and $C_{5'}$/$C_{8'}$) of the HOMO of 2-fluorodihydroanthracene **11d** are not equivalent with respect to the mirror plane, deriving greatly from the higher-lying HOMO of fluorobenzene (PM3: −9.806 eV) rather than the HOMO of benzene (PM3: −9.751 eV). Although these asymmetric amplitudes allow the interaction of the HOMO of **11d** with the π orbital of the ethylene (π_{CC}), incomplete phase agreement between these π fragments greatly diminishes the effect. A smaller bias (*syn* preference) observed in the fluoro derivative (**1d**) as compared with the nitro derivative (**1b**) may be interpreted in terms of the cancellation owing to the interaction with the HOMO of the fluorodihydroanthracene (**11d**) (*anti*-preference).

Scheme 3. Distortion of the Carbonyl π* Orbital



Orbital Interaction Motifs in the Reduction of the Carbonyl Group. Reduction of a carbonyl group with a reducing reagent involves interaction of the vacant π orbital of the carbonyl group (π_{CO}*, LUMO) with the occupied orbital of the hydride ion. The orbitals of the substituted dibenzobicyclo[2.2.2]octadienones (**2** and **3**) are also assumed to be constructed from orbitals of subsystems (**9** and **10**, Figure 4), i.e., the substituted dihydroanthracene **11** in convex geometry and the carbonyl group (formaldehyde, for simplicity). Coefficients of LUMO's and NXLUMO's for substituted dihydroanthracenes **11a**–**d** were obtained by means of semiempirical PM3 methods[23] and are shown in Chart 2. There are two orientations in the combination of the π* orbitals of the carbonyl group with the aromatic π orbitals of **11**, i.e., as in 2-substituted (**2**) and 3-substituted dibenzobicyclo[2.2.2]octadienones (**3**), respectively (**9** and **10**). The low-lying vacant orbitals of **11** bearing components at the *ipso* (C-1′ ,C-4′, C-5′, and C-8′) positions can participate in the mixing with the π^*_{CO} orbital. An electron-withdrawing substituent such as a nitro or a fluoro group perturbs the π face of the carbonyl group (case c in Table 1). As shown in Chart 2, the LUMO's of the dihydroanthracenes substituted with an electron-withdrawing nitro (**11b**) or fluoro group (**11d**) have coefficients largely localized on the benzene ring bearing a nitro or a fluoro group, respectively, because the LUMO (PM3: −1.084 eV) of **11b** is predominantly derived from the LUMO of nitrobenzene (PM3: −1.1332 eV), significantly lower in energy than the LUMO of benzene (PM3: 0.396 eV, degenerate), and the LUMO (PM3: −0.022 eV) of fluorodihydroanthracene **11d** can also be analyzed as a derivative of the LUMO of fluorobenzene (PM3: 0.027 eV), lower in energy than the LUMO of benzene (PM3: 0.396 eV). Owing to orbital phase agreement and similar energy, the π^*_{CO} orbital (the LUMO of formaldehyde, 0.825 eV, PM3) mixes preferentially with the LUMO's of **11b** and **11d** at the *ipso* position at C-4′ (for the systems **2** and **3**) in an in-phase manner (**9** and **10** in Figure 4) (Scheme 3). This in-phase mixing lowered the energy of the π^*_{CO} fragment, activating it for attack of a nucleophile. Simultaneously, the in-phase overlap results in buildup of a virtual bonding region between nuclei. Therefore, the π^*_{CO} fragment favors the interaction with the HOMO of the hydride ion on the side of the substituent, resulting in the biased reduction product (*anti* alcohols) observed in the 2- and 3-nitro derivatives (**2b** and **3b**) and the 2- and 3-fluoro derivatives (**2d** and **3d**). Although there could be a difference in regioselectivity of **2b** and **3b** owing to the different ampulitudes of $C_{1'}$ and $C_{4'}$ of the LUMO of **11b**, the coefficients largely localized on the benzene ring bearing a nitro group build up the bonding region of the π^*_{CO} fragment *exclusively* on the side of the substituent in both cases, accounting for the observed similar bias. On the other hand, the LUMO (+0.225 eV) of the dihydroanthracene substituted with an electron-donating hydroxy group (**11c**) bears the orbital amplitudes at the *ipso* (C-1′ and C-4′; C-5′ and C-8′) positions, approximately symmetric in sign and in magnitude with respect to the plane passing through C-9 and C-10 (Chart 2). The NXHOMO (0.294 eV) of **11c** is also symmetric in sign. Therefore, the antisymmetric π^*_{CO} orbital does not interact significantly with these vacant π orbitals of **11c**, resulting in an unperturbed π face of the carbonyl π* orbital. This motif is regarded as an example of orbital *non*interaction, designated as case e in Table 1. Thus, the reduction of 2-methoxy- and 3-methoxydibenzobicyclo[2.2.2]octadienones (**2c** and **3c**) should intrinsically show little or no bias, although the slight *anti* attack preference of **2c** is not explained by this model.

Conclusion

We have described biased reactions in dibenzobicyclo[2.2.2]octatrienes and dibenzobicyclo[2.2.2]octadienones and also analyzed the orbital interaction motif within the frontier orbital frameworks[28] on the basis of the first-order interactions of the π orbital of the olefin and the π* orbital of the carbonyl with the aromatic π orbitals.[29] As we have pointed out in the text, the observed biases are divergent in the dibenzobicyclo[2.2.2]octane derivatives and our previous aromatic systems, spiro[cyclopentane-1,9′-fluorene] derivatives, which do not reflect the conventional electronic substituent effect.[3] Our proposed orbital interaction motif allows a unified interpretation of the orbital distortions in these divergent conjugation systems. The unsymmetrization of the π (or π*) lobes arising from the asymmetrical environment stems from the orbital density change in the internuclear regions. This simultaneously involves constructive and destructive orbital interference of the wave function. A computational idea, proposed by Dannenberg et al.,[28] involving introduction of Guaussian s functions superimposed over each lobe of the p-function of π orbitals may represent the orbital interference (orbital diffusion) in the internuclear region of interactive fragment orbitals.

Experimental Section

General Methods. All the melting points were measured with a Yanagimoto hot-stage melting point apparatus (MP-500) and are uncorrected. Proton NMR spectra were measured

(28) Huang, X. L.; Dannenberg, J. J.; Duran, M.; Bertran, J. *J. Am. Chem. Soc.* **1993**, *115*, 4024–4030. Huang, X. L.; Dannenberg, J. J. *J. Am. Chem. Soc.* **1993**, *115*, 6017–6024.

(29) A possible explanation for the bias was proposed based on geometrical distortions of the molecular skeletons (Wipff, G.; Morokuma, K. *Tetrahedron Lett.* **1980**, *21*, 4445–4448. Watson, W.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022–2031. Spanget-Larsen, J.; Gleiter, R. *Tetrahedron Lett.* **1982**, *23*, 2435–2438. Gleiter, R.; Spanget-Larsen, J. *Tetrahedron* **1983**, *39*, 3345–3350. Koga, N.; Ozawa, T.; Morokuma, K. *J. Phys. Org. Chem.* **1990**, *3*, 519–533). Skeletal distortion such as pyramidalization of double bonds (i.e., out-of-plane deformation) in norbornene derivatives has been suggested so far. However, no significant geometrical distortion such as pyramidalization of the olefin and carbonyl centers or tilting of the ethano bridge (*vide infra*) has been detected by X-ray crystallographic analysis of the nitro compounds (**1b**, **2b**, and **3b**). A close scrutiny showed a small but discrete tilting of the ethano bridge in these nitro dibenzobicyclic compounds: tilting of the ethano bridge plane ($C_9C_{12}C_{11}C_{10}$) toward one of the benzene planes in a similar manner to the hinge of a fan: the differences of hinge angles ($\angle C_8C_9C_{12}$ and $\angle C_1C_9C_{12}$) are **1b**, +4.3 °, **2b**, +7.7°, **3b**, −3.5 ° (a positive (negative) sign indicates a tilting, departing from (approaching) the nitro benzene plane). The details of the X-ray crstallographic analysis will be published elsewhere (Dr. Kentaro Yamaguchi, Chiba Univesity). These nitro compounds (**1b**, **2b**, and **3b**) all exhibited a large bias in reactions, in favor of the *syn* addition of the reagents. However, the directions of the tilting of the ethano bridge are different, despite the observed *syn* addition in all cases. Therefore, the geometrical tilting is not likely to be the cause of the observed bias.

on a JEOL GX 400-MHz NMR spectrometer with TMS as an internal reference in $CDCl_3$ as the solvent. High-performance liquid chromatography (HPLC) was run on a Shimadzu LC-6A system on LiChrosorb Si60 (Merck) packing (8 mm × 25 cm) or on silica gel SIL S-5 (SH-043-5, YMC, Japan) packing (20 mm × 25 cm) with ethyl acetate and *n*-hexane as the eluents. Flash column chromatography was performed on silica gel (Kieselgel 60, 230–400 mesh, Merck) with the specified solvent.[30] The combustion analyses were carried out in the microanalytical laboratory of this institution.

Preparation of Dibenzobicyclo[2.2.2]octatriene (9,10-Dihydro-9,10-ethenoanthracene).[11] (A) Preparation of Dimethyl 9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylate. A mixture of 26.78 g of anthracene and 38.34 g (1.8 equiv) of dimethyl acetylenedicarboxylate was heated at 140 °C for 6.5 h, followed by recrystallization (37.9 g, 79% yield), mp 160–161 °C (colorless prisms, recrystallized from methanol). Mass: (*m/e*) 320 (M^+). Anal. Calcd for $C_{20}H_{16}O_4$: C, 74.99; H, 5.03. Found: C, 74.97; H, 5.01.

(B) Hydrolysis of the Diester to 9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylic Acid. To a solution of the diester (19.2 g, obtained above) in methanol (250 mL) was added aqueous NaOH (2 N) (400 mL), and the mixture was heated at 60 °C for 3 h, followed by acidification with aqueous HCl (2 N) to give 16.29 g (93%) of the diacid after collection, mp 247.5–250 °C. Mass: (*m/e*) 292 (M^+).

(C) Decarbonylation of the Diacid. A mixture of 16.29 g of the above diacid and 3.18 g (0.9 equiv) of copper powder in 36 mL of quinoline was heated at 240 °C in an oil bath over 1 h. The reaction mixture was filtered to remove the copper powder and extracted with methylene chloride, followed by washing with aqueous HCl, aqueous NaOH, and brine. The residue after evaporation was flash-chromatographed with *n*-hexane to give 7.12 g (63%) of dibenzobicyclo[2.2.2]octatriene (9,10-dihydro-9,10-ethenoanthracene) (**1a**), mp 120.5–122.5 °C (colorless prisms, recrystallized from hexane). Mass: (*m/e*) 204 (M^+). Anal. Calcd for $C_{16}H_{12}$: C, 94.08; H, 5.92. Found: C, 94.01; H, 5.95.

Preparation of 2-Nitrodibenzobicyclo[2.2.2]octatriene (2-Nitro-9,10-dihydro-9,10-ethenoanthracene) (1b). (A) Nitration of Dimethyl 9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarboxylate. Acetic anhydride (5 mL) was added in one portion to a weighed amount of fuming HNO_3 (198 mg, 93%, 1.5 equiv) at −43 °C (acetonitrile–dry ice).[31] The mixture was stirred at −43 °C for 3 min, and then 5 mL of methylene chloride was added to dilute the nitrating reagent. At −43 °C, the precursor diester (669 mg) was added. After being stirred at −43 °C for 8 h, the whole mixture was added to 100 mL of ice and water and extracted with methylene chloride. Evaporation of the solvent gave a residue (790 mg), which was flash-chromatographed (ethyl acetate:*n*-hexane 1:5) to give 605 mg (78%) of dimethyl 2-nitro-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate, mp 168.5–170 °C (pale yellow cubes, recrystallized from *n*-hexane and methylene chloride). Mass: (*m/e*) 365 (M^+). Anal. Calcd for $C_{20}H_{15}NO_6$: C, 65.75; H, 4.14; N, 3.83. Found: C, 65.45; H, 4.14; N, 3.93.

(B) Decarbonylation. Hydrolysis of the nitro diester obtained in A and subsequent decarbonylation as described in the case of **1a** gave 2-nitrodibenzobicyclo[2.2.2]octatriene (2-nitro-9,10-dihydro-9,10-ethenoanthracene) (**1b**) in 44% yield, mp 186–189 °C (pale yellow prisms, recrystallized from CH_2Cl_2–hexane). Mass: (*m/e*) 249 (M^+). Anal. Calcd for $C_{16}H_{11}NO_2$: C, 77.10; H, 4.45; N, 5.62. Found: C, 77.12; H, 4.40; N, 5.89.

Preparation of 2-Methoxydibenzobicyclo[2.2.2]-octatriene (2-Methoxy-9,10-dihydro-9,10-ethenoanthracene) (1c). (A) Reduction of the Nitro Derivative 1b. A solution of **1b** (125 mg) in ethanol was heated under gentle reflux in the presence of diluted aqueous HCl (0.5N, 1 mL) and iron powder (447 mg) with vigorous stirring. After 1 h, the cold mixture was poured into saturated aqueous sodium bicarbonate and extracted with methylene chloride. The residue was flash-chromatographed (ethyl acetate:*n*-hexane 1:5) to give 97 mg (78%) of 2-aminodibenzobicyclo[2.2.2]-octatriene.

(B) Diazotization and Hydrolysis to 2-Hydroxydibenzobicyclo[2.2.2]octatriene. A solution of 2-aminodibenzobicyclo[2.2.2]octatriene (2.10 g) in 25 mL of acetic acid was treated at 18 °C with concentrated sulfuric acid (6 mL), followed by the addition of an aqueous solution of sodium nitrate (927 mg) in 7 mL of water over 5 min. After the mixture was stirred at 18 °C for 15 min, urea (324 mg) and 30 mL of ice and water were added. The resultant solution of the diazonium ion was added in portions to a preheated (to gentle reflux) solution of concentrated sulfuric acid (9 mL) in 50 mL of water over 20 min. After being heated for another 10 min, the mixture was extracted with methylene chloride. The crude residue (2.11 g) was flash-chromatographed (ethyl acetate:*n*-hexane 1:8) to give 1.57 g (72%) of 2-hydroxydibenzobicyclo[2.2.2]octatriene. Mass: (*m/e*) 220 (M^+).

(C) Methylation. The phenol (1.57 g) obtained above was dissolved in aqueous 3 N NaOH (50 mL), and dimethyl sulfate (19 mL, 20 equiv) was added at ambient temperature. A slight exothermic reaction took place. The reaction mixture was heated at 55 °C for 15 min and was extracted with methylene chloride. The residue was flash-chromatographed (ethyl acetate:*n*-hexane 1:30) to give 1.53 g (90%) of 2-methoxydibenzobicyclo-[2.2.2]octatriene (2-methoxy-9,10-dihydro-9,10-ethenoanthracene) (**1c**), mp 92–94.5 °C (colorless prisms, recrystallized from CH_2Cl_2–hexane). Mass: (*m/e*) 234 (M^+). Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.97; H, 6.04.

Preparation of 2-Fluorodibenzobicyclo[2.2.2]octatriene (2-Fluoro-9,10-dihydro-9,10-ethenoanthracene) (1d). 2-Fluorodibenzobicyclo[2.2.2]octatriene (**1d**) was prepared from 2-fluoroanthracene[12] in a manner similar to the parent **1a**. **1d**: mp 128–129.2 °C (colorless cubes, recrystallized from *n*-hexane). Anal. Calcd for $C_{16}H_{11}F$: C, 86.46; H, 4.99. Found: C, 86.70; H, 4.95.

Preparation of Dibenzobicyclo[2.2.2]octadienone (9,-10-Dihydro-11-keto-9,10-ethanoanthracene) (2a). Dibenzobicyclo[2.2.2]octadienone (**2a**) was prepared as previously described with the following modification: **2a** was prepared by the Oppenauer oxidation of the corresponding alcohol, 9,-10-dihydro-11-hydroxy-9,10-ethanoanthracene. Aluminum tributoxide (988 mg, 2 equiv) was added to a solution of the alcohol (444 mg) and *p*-quinone (258 mg, 1.2 equiv) in benzene (20 mL) at room temperature. The mixture was refluxed at 93 °C (external) for 14 h. The reaction mixture was straightforwardly flash-chromatographed (ethyl acetate:*n*-hexane 1:3) to give the ketone **2a** (402 mg, 91%) after recrystallization. **2a**: mp 154.3–154.5 °C (colorless plates, recrystallized from *n*-hexane). Anal. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 87.14; H, 5.50.

Nitration of Dibenzobicyclo[2.2.2]octadienone (Preparation of 2-Nitro- and 3-Nitro-9,10-dihydro-11-keto-9,10-ethanoanthracenes). Dibenzobicyclo[2.2.2]octadienone (**2a**) (111 mg) was nitrated with the reagent prepared from fuming HNO_3 (81.7 mg, 94%, 2.5 equiv) and acetic anhydride (1 mL) in 1 mL of methylene chloride at 3 °C (an ice–water bath) for 8.5 h. The organic phase was extracted with methylene chloride, and the extract was washed with saturated aqueous sodium bicarbonate and brine. Evaporation gave a pale yellow solid (119 mg, 89%). The ratio of the isomers was estimated to be 1:1 (**2b**:**3b**) based on integration of the proton signals in the ^1H NMR spectrum. The mixture was separated by flash-chromatography (ethyl acetate:*n*-hexane 1:5). A lower reaction temperature did not alter the isomer distribution. At −22 °C (carbon tetrachloride–dry ice) the nitration of **2a** gave 14% of **2b** and 14% of **3b**, together with recovered **2a** (58%), after flash-chromatography (ethyl acetate–*n*-hexane 1:12). 2-Nitro-9,10-dihydro-11-keto-9,10-ethanoanthracene (**2b**): mp 210–211.5 °C (pale yellow cubes, recrystallized from *n*-hexane). Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.44; H, 4.18; N, 5.28. Found: C, 72.18; H, 4.15; N, 5.20. 3-Nitro-9,10-dihydro-11-keto-9,10-ethanoanthracene (**3b**): mp 163–164 °C (colorless plates, recrystallized from *n*-hexane). Anal. Calcd for

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$C_{16}H_{11}NO_3$: C, 72.44; H, 4.18; N, 5.28. Found: C, 72.27; H, 4.23; N, 5.03.

Preparation of 2-Methoxydibenzobicyclo[2.2.2]octadienone (2-Methoxy-9,10-dihydro-11-keto-9,10-ethanoanthracene) (2c). The methoxy ketone **2c** was prepared in a manner similar to the methoxy olefin **1c**, starting from the 2-nitro ketone **2b** through hydrogenation (quantitative yield) over Pd carbon in ethyl acetate, diazotization, hydrolysis (61% yield), and methylation (78% yield). **2c**: mp 131.5–133 °C (colorless cubes, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.57; H, 5.63. Found: C, 81.44; H, 5.64.

Preparation of 3-Methoxydibenzobicyclo[2.2.2]octadienone (3-Methoxy-9,10-dihydro-11-keto-9,10-ethanoanthracene) (3c). 3-Methoxy-9,10-dihydro-11-keto-9,10-ethanoanthracene (**3c**) was prepared from the corresponding nitro compound **3b** in a similar manner to **2c**. **3c**: mp 103–104 °C (colorless plates, recrystallized from *n*-hexane). Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.57; H, 5.63. Found: C, 81.27; H, 5.62.

Preparation of 2-Fluorodibenzobicyclo[2.2.2]octadienone (2-Fluoro-9,10-dihydro-11-keto-9,10-ethanoanthracene) (2d). 2-Fluoro-9,10-dihydro-11-keto-9,10-ethanoanthracene (**2d**) was prepared from the 2-nitro ketone **2b** through hydrogenation (89% yield) and Siemann reaction (50% yield).[14] **2d**: mp 119–121.5 °C (white powder, recrystallized from *n*-hexane). Anal. Calcd for $C_{16}H_{11}OF$: C, 80.65; H, 4.65. Found: C, 80.59; H, 4.59.

Preparation of 3-Fluorodibenzobicyclo[2.2.2]octadienone (3-Fluoro-9,10-dihydro-11-keto-9,10-ethanoanthracene) (3d). 3-Fluoro-9,10-dihydro-11-keto-9,10-ethanoanthracene (**3d**) was prepared from the corresponding 3-nitro ketone **3b** through hydrogenation (76% yield) and Siemann reaction (42% yield).[14] **3d**: mp 133.5–135.5 °C (colorless plates, recrystallized from *n*-hexane). Anal. Calcd for $C_{16}H_{11}OF$: C, 80.65; H, 4.65. Found: C, 80.65; H, 4.92.

Epoxidation of Dibenzobicyclo[2.2.2]octatriene (1a). Dibenzobicyclo[2.2.2]octatriene (**1a**) (102 mg) was added in one portion to a solution of *m*-CPBA (185 mg, 70%, 1.5 equiv) in 1.5 mL of chloroform at 3 °C (ice and water). The mixture was stirred at 3 °C for 41 h and then poured into aqueous (2 N) sodium carbonate and extracted with methylene chloride. The residue was flash-chromatographed (ethyl acetate:*n*-hexane 1:8) to give 97 mg (88%) of the epoxide **4a**. Epoxide of **1a** (**4a**): mp 174.5–175.5 °C (colorless needles, recrystallized from *n*-hexane/methylene chloride). Mass: (*m/e*) 220 (M^+). Anal. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 87.34; H, 5.35.

Epoxidation of Substituted Dibenzobicyclo[2.2.2]octatrienes. Epoxidation of substituted dibenzobicyclo[2.2.2]-octatrienes **1b–d** was carried out at 3 °C for the specified time (Table 2) in the same manner as described for **1a**. Yields and ratios of the diastereomers were determined from ^1H NMR spectra after separation of the products (as a mixture) by flash column chromatography with a specified solvent. The mixtures of the diastereomeric epoxides were separated by repeated flash-column chromatography. Pure diastereomers were analyzed by ^1H NMR spectroscopy. The assignments of the ^1H NMR signals were based on INDOR (internuclear double resonance) measurements.

Epoxidation of 2-Nitrodibenzobicyclo[2.2.2]octatriene (1b). A crude mixture of the epoxides (77% yield, after 212 h at 3 °C) was obtained by flash-column chromatography (ethyl acetate:*n*-hexane 1:12). Diastereomers were separated by repeated flash column chromatography (ethyl acetate:*n*-hexane 1:12). *Syn* epoxide of **1b** (**4b-*syn***): mp 196–205 °C (pale yellow cubes, recrystallized from benzene). Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.44; H, 4.18; N, 5.28. Found: C, 72.24; H, 4.26; N, 5.21. *Anti* epoxide of **1b** (**4b-*anti***): mp 247–251 °C (pale yellow cubes, recrystallized from benzene). Anal. Calcd for $C_{16}H_{11}NO_3$: C, 72.44; H, 4.18; N, 5.28. Found: C, 72.50; H, 4.21; N, 5.52.

Epoxidation of 2-Methoxydibenzobicyclo[2.2.2]octatriene (1c). A crude mixture of the epoxides (63% yield, after 46 h at 3 °C) was obtained by flash-column chromatography (ethyl acetate:*n*-hexane 1:8). Diastereomers were separated by flash-column chromatography (methylene chloride:*n*-hexane 1:2). *Syn* epoxide of **1c** (**4c-*syn***): mp 112.5–113.5 °C (colorless cubes, recrystallized from *n*-hexane). Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.46; H, 5.63. *Anti* epoxide of **1c** (**4c-*anti***): oily material.

Epoxidation of 2-Fluorodibenzobicyclo[2.2.2]octatriene (1d). The diastereomers were obtained as a mixture by flash column chromatography (methylene chloride:*n*-hexane 1:2), and the mixture was separated by HPLC with ethyl acetate:*n*-hexane (1:120) as the eluent. *Syn* epoxide of **1d** (**4d-*syn***): mp 153.5–154.5 °C (colorless powder, recrystallized from *n*-hexane). Anal. Calcd for $C_{16}H_{11}FO \cdot {}^1/_3H_2O$: C, 78.67; H, 4.82. Found: C, 78.90; H, 4.67. *Anti* epoxide of **1d** (**4d-*anti***): mp 169.6–172 °C (colorless needles, recrystallized from *n*-hexane). Anal. Calcd for $C_{16}H_{11}FO \cdot {}^1/_6H_2O$: C, 79.67; H, 4.52. Found: C, 79.65; H, 4.74.

Dihydroxylation of Dibenzobicyclo[2.2.2]octatriene (1a) by Osmium Tetraoxide. The triene **1a** (122 mg) was added to a solution of osmium tetraoxide (160 mg, 1.1 equiv) in pyridine (2.5 mL) at −27 °C, and the resultant orange solution was stirred for 5 h. A mixture of aqueous solution of sodium bisulfite (280 mg, 58%, 2.6 equiv) in 5 mL of water and pyridine (3 mL) was added to quench the reaction. After being stirred at room temperature, the reaction mixture was extracted with methylene chloride. The residue obtained after evaporation was flash-chromatographed (ethyl acetate:*n*-hexane 1:3) to give 128 mg (90%) of the diol of **1a** (**5a**). Diol of **1a** (**5a**): mp 210.5–211 °C (colorless cubes, recrystallized from benzene). Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.39; H, 5.92.

Oxidation of 1a with Potassium Permanganate. An aqueous solution of potassium permanganate (81 mg, 1.5 equiv) in 12 mL of water was added dropwise to a solution of **1a** (102 mg) in 6 mL of pyridine at −14 °C (ice–salt bath) over 30 min. After the addition, the reaction mixture was treated with sodium bisulfite (180 mg) and was extracted with methylene chloride. The residue obtained was flash-chromatographed (ethyl acetate–*n*-hexane 1:6) to give the diol **5a** in 58% yield and anthraquinone in 22% yield.

The diol **5a** was converted to the dimethyl acetal with acetone: a large excess of dry acetone (1.16 g) and a catalytic amount of *p*-toluenesulfonic acid (4 mg) were added to a solution of 29 mg of **5a** in dry benzene (4 mL). The solution was heated at reflux under a Dean–Stark trap for 1 h. After evaporation of the solvent, the resultant residue was flash-chromatographed (ethyl acetate:*n*-hexane 1:9) to give 25 mg (80%) of the dimethyl acetal of the diol **5a**. Dimethyl acetal of diol of **1a** (**5a**): mp 140.5–141 °C (colorless cubes, recrystallized from hexane). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52. Found: C, 81.76; H, 6.57.

Dihydroxylation of 2-Nitrodibenzobicyclo[2.2.2]octatriene (1b). The diastereomers, obtained by dihydroxylation with osmium tetraoxide in a similar manner to **1a**, were separated by repeated flash column chromatography (ethyl acetal:*n*-hexane 1:3). *Syn* diol of **1b** (**5b-*syn***): 233.5–234 °C (pale yellow cubes, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.91. Found: C, 67.96; H, 4.59; N, 5.22. *Anti* diol of **1b** (**5b-*anti***): 215–216.5 °C (colorless needles, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{16}H_{13}NO_4$: C, 67.84; H, 4.63; N, 4.91. Found: C, 67.54; H, 4.64; N, 5.01.

The dimethyl acetal of **5b-*syn*** was prepared in a similar manner to the dimethyl acetal of the diol **5a**. Dimethyl acetal of the *syn* diol of **1b** (**5b-*syn***): mp 256.5–257 °C (colorless cubes, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{19}H_{17}NO_4$: C, 70.58; H, 5.30; N, 4.33. Found: C, 70.42; H, 5.92; N, 4.39.

Dihydroxylation of 2-Methoxydibenzobicyclo[2.2.2]-octatriene (1c). The diastereomers of the diols were obtained by dihydroxylation with osmium tetroxide at −27 °C for 1.5 h. No adequate solvent for separating the mixture of diastereomers could be found. However, we were able to separate the diastereomers after the formation of dimethyl acetals with acetone: a solution of **5c** (73.7 mg, a mixture), *p*-toluenesulfonic acid (8 mg), and dry acetone (1 mL) in benzene (4 mL) was heated at 75 °C for 1.5 h. Evaporation of the solvent gave a residue (98.7 mg) which was flash-chromatographed (meth-

ylene chloride:*n*-hexane 1:2) to give the pure acetal of **5c-*syn*** (29.2 mg) and a mixture (46.8 mg) of the acetals of **5c-*syn*** and **5c-*anti*** (a major component). The crude **5c-*anti*** was fractionally recrystallized from *n*-hexane. Dimethyl acetal of the *syn* diol of **1c** (**5c-*syn***): mp 108.5–109 °C (colorless fine needles, recrystallized from *n*-hexane). Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.88; H, 6.54. Dimethyl acetal of the *anti* diol of **1c** (**5c-*anti***): mp 140.5–141.5 °C (colorless fine needles, recrystallized from *n*-hexane). Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.90; H, 6.60.

Dihydroxylation of 2-Fluorodibenzobicyclo[2.2.2]octatriene (1d). The diastereomers (49.4 mg) were separated by HPLC with ethyl acetate:*n*-hexane (1:6) as the eluent. *Syn* diol of **1d** (**5d-*syn***): mp 213–214 °C (colorless plates, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{16}H_{13}FO_2$: C, 74.99; H, 5.11. Found: C, 75.01; H, 5.05. *Anti* diol of **1d** (**5d-*anti***): mp 162–163.5 °C (colorless fine cubes, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{16}H_{13}FO_2$: C, 74.99; H, 5.11. Found: C, 74.68; H, 5.09. The *syn* diol **5d-*syn*** was converted to the dimethyl acetal with acetone by a usual method (acetone/*p*-toluenesulfonic acid) in the yield of 92%. Dimethyl acetal of the *syn* diol of **1d** (**5d-*syn***): mp 187–188 °C (colorless cubes, recrystallized from *n*-hexane). Anal. Calcd for $C_{19}H_{17}FO_2 \cdot {}^1/_6H_2O$: C, 76.23; H, 5.84. Found: C, 76.37; H, 5.66.

Reduction of Dibenzobicyclo[2.2.2]octadienone (2a). Sodium borohydride (17.3 mg, 90%, 3.4 equiv) was added in one portion to a solution of the ketone **2a** (26.2 mg) in 5 mL of dry methanol at −43 °C (acetonitrile–dry ice). After the mixture was stirred for 2 h, ice and water were added. The solvent was evaporated, and the residue was extracted with methylene chloride (50 mL). The extract was dried over Na_2SO_4 and evaporated to give the pure alcohol (24.6 mg, 93%) (**6a** = **7a**). Its NMR spectra were in good accordance with those of an authentic sample.[13]

Reduction of 2- and 3-Substituted Dibenzobicyclo[2.2.2]octadienones. Substituted dibenzobicyclo[2.2.2]octadienones (typically 25 mg) were reduced with sodium borohydride (90%, 4 equiv) in ethanol (5 mL) at −43 °C (acetonitrile–dry ice) for a specified time (Table 3). The yields and ratios of the diastereomers were determined from the ^1H NMR spectra after separation of the products (as a mixture) by flash-column chromatography (ethyl acetate/*n*-hexane 1:2 or 1:4). Diastereomers were isolated by flash column chromatography and/or high-performance liquid chromatography (packed with silica gel) with specified solvents. Pure diastereomers were analyzed by thin-layer chromatography (on TLC plates precoated with silica gel $60F_{254}$ (layer thickness 0.25 mm, Merck) and glass plates coated with silica gel $60GF_{254}$ (Merck)) and by ^1H NMR spectroscopy. The assignments of the ^1H NMR signals (in particular, those of aromatic protons) are based on INDOR (internuclear double resonance) and NOE measurements.

Reduction of 2-Nitrodibenzobicyclo[2.2.2]octadienone 2b. The diastereomers (obtained from 99.9 mg of the ketone **2b**) were separated by flash column chromatography (ethyl acetate:*n*-hexane 1:3) to give 14.2 mg of pure **6b-*syn*** (a less polar isomer) and a crude fraction of **6b-*anti*** (50.6 mg). The latter fraction was again flash-chromatographed (methylene chloride:*n*-hexane 2:1) to give pure **6b-*anti*** (30.4 mg). *Syn* alcohol of **2b** (**6b-*syn***): mp 133.5–134 °C (colorless cubes, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.77; H, 4.92; N, 5.30. *Anti* alcohol of **2b** (**6b-*anti***): mp 190–191 °C (colorless fine needles, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.64; H, 4.91; N, 5.15.

Reduction of 2-Methoxydibenzobicyclo[2.2.2]octadienone (2c). The diastereomers (obtained from 52.4 mg of the ketone **2c**) were separated by high-performance liquid chromatography (Lichrosorb Si60) with ethyl acetate:*n*-hexane (1:6) as the eluent. *Syn* alcohol of **2c** (**6c-*syn***): mp 140.5–141 °C (colorless cubes, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.62; H, 6.42. *Anti* alcohol of **2c** (**6c-*anti***): mp 167–168 °C (colorless needles, recrystallized from *n*-hexane). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.66; H, 6.44.

Reduction of 2-Fluorodibenzobicyclo[2.2.2]octadienone (2d). The diastereomers (obtained from 23.8 mg of the ketone **2d**) were separated by high-performance liquid chromatography (Lichrosorb Si60) with ethyl acetate:*n*-hexane (1:8) as the eluent. *Syn* alcohol of **2d** (**6d-*syn***): mp 145.5–146 °C (white powder, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{16}H_{13}FO$: C, 79.98; H, 5.45. Found: C, 79.89; H, 5.41. *Anti* alcohol of **2d** (**6d-*anti***): mp 123.5–124.5 °C (colorless plates, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{16}H_{13}FO$: C, 79.98; H, 5.45. Found: C, 79.98; H, 5.45.

Reduction of 3-Nitrodibenzobicyclo[2.2.2]octadienone (3b). The diastereomers (obtained from 10.1 mg of **3b**) were separated by flash column chromatography (ethyl acetate:*n*-hexane 1:4) to give 2.4 mg of pure **7b-*syn*** and 5.0 mg of crude **7b-*anti***. The latter fraction was further flash-chromatographed (methylene chloride) to give 2.0 mg of pure **7b-*syn***. *Syn* alcohol of **3b** (**7b-*syn***): mp 140.0–141.5 °C (colorless cubes, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.74; H, 5.00; N, 5.30. *Anti* alcohol of **3b** (**7b-*anti***): mp 239–240 °C (colorless cubes, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.99; H, 4.93; N, 5.34.

Reduction of 3-Methoxydibenzobicyclo[2.2.2]octadienone (3c). The diastereomers (obtained from 25.0 mg of the ketone **3c**) were separated by high-performance liquid chromatography (Lichrosorb Si60) with ethyl acetate:*n*-hexane (1:6) as the eluent. *Syn* alcohol of **3c** (**7c-*syn***): mp 143–144 °C (colorless needles, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.75; H, 6.35. *Anti* alcohol of **3c** (**7c-*anti***): mp 104.5–106 °C (colorless fine needles, recrystallized from *n*-hexane). Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 80.62; H, 6.62.

Reduction of 3-Fluorodibenzobicyclo[2.2.2]octadienone (3d). The diastereomers (obtained from 28.9 mg of **3d**) were separated by high-performance liquid chromatography (Lichrosorb Si60) with ethyl acetate:*n*-hexane (1:15) as the eluent. *Syn* alcohol of **3d** (**7d-*syn***): mp 151–152 °C (white powder, recrystallized from *n*-hexane). Anal. Calcd for $C_{16}H_{13}FO \cdot {}^1/_6H_2O$: C, 78.99; H, 5.52. Found: C, 79.22; H, 5.32. Anti alcohol of **3d** (**7d-*anti***): mp 127.5–128 °C (colorless needles, recrystallized from *n*-hexane/CH_2Cl_2). Anal. Calcd for $C_{16}H_{13}FO$: C, 79.98; H, 5.45. Found: C, 79.79; H, 5.36.

Calculational Methods. The calculations have been performed at the Computer Center of the University of Tokyo. PM3 calculations were carried out by using the MOPAC program systems (version 6.02).[32,33] Geometry optimizations were performed with the standard Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm incorporated in the program. Structures of dihydroanthracenes **11a–d** were optimized without restriction of symmetry except C_s symmetry of the aromatic rings.

Supplementary Material Available: ^1H NMR data for obtained compounds (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

(32) MOPAC (version 6.0): Stewart, J. J. P. QCPE program no. 455.
(33) Revised as MOPAC (version 6.01 and 6.02) by Prof. Tsuneo Hirano, Ochanomizu University, for HITAC version, *JCPE Newsletter* **1991**, *2*, 26.