Pericyclic Reaction Behavior of Cyclopentadienones toward Acyclic Conjugated Dienes. [3,3]-Sigmatropic Rearrangement and Double Diels–Alder Reactions of the *endo*[4+2]π Cycloadducts

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Cycloaddition of 2,5-disubstituted-3,4-diphenylcyclopentadienone with acyclic conjugated dienes gave the *endo* [4+2]π cycloadducts, which then underwent [3,3]-sigmatropic rearrangement to give the corresponding *endo* [2+4]π cycloadduct on heating at 110 °C. Pyrolysis of the *endo* [4+2]π cycloadducts at 170 °C resulted in decarbonylation to give the double Diels–Alder adduct. The sequential pericyclic reaction behavior is discussed on the basis of X-ray diffraction analyses and molecular orbital calculation data.

Key words cyclopentadienone; 1,3-alkadiene; double Diels–Alder reaction; [3,3]-sigmatropic rearrangement; *ab initio* calculation; X-ray analysis

It is well known that the *endo* [4+2]π cycloadducts (Diels–Alder (DA) adduct) of cyclopentadienones and medium-membered cyclic polyenes such as cycloheptatriene undergo [3,3]-sigmatropic rearrangement ([3,3]) to give the [2+4]π cycloadducts,[1] and the rearrangement rates are so rapid that the primary [4+2]π cycloadducts generally can not be isolated.[1d] In contrast, the [4+2]π cycloadducts of linear polyenes are thermally stable and hardly undergo [3,3]-sigmatropic rearrangement to give the [2+4]π cycloadducts. The observed reactivity difference between the two can be ascribed to the inherent nature of the ground-state geometries of the [4+2]π cycloadducts.

In the course of a study on synthetic design using sequential pericyclic reactions, we found that the reaction of cyclopentadienones with ethyl sorbate gave the double Diels-Alder (DDA) adduct (**5**) *via* three-step sequential pericyclic reactions [addends → DA adduct (**3**) → decarbonylated DA adduct (**4**) → intramolecular DA (IMDA) adduct (**5**)], and lowering of the reaction temperature or the use of phenolic compounds as a solvent afforded the [3,3]-sigmatropic rearrangement product (**6**), together with the DDA adduct.

In connection with this, we have examined the solvent effect of phenols on the pericyclic reaction of 2,5-bis-(methoxycarbonyl)-3,4-diphenylcyclopentadienone (**1a**) with ethyl sorbate (**2a**).[2] The reactions are discussed here in the light of newly obtained data to clarify the overall character of the reactions.

Results

Theoretical Calculations To examine the feasibility of [3,3]-sigmatropic rearrangement of the DA cycloadducts of cyclopentadienone and open-chain conjugated dienes, we performed *ab initio* calculations[3] on the [3,3]-sigmatropic rearrangement reaction of the *endo* DA cycloadduct. To reduce computation time, the calculations were performed on the thermal behaviors of the DA adducts derived from the parent cycloaddition reaction of cyclopentadienone and butadiene. The calculation data are summarized in Tables 1a and 1b. The MP2/6-31G* calculated geometries of the reactants and transition

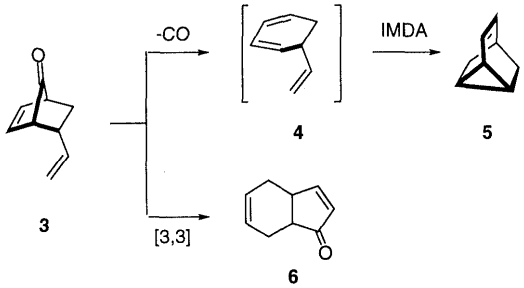

Chart 2

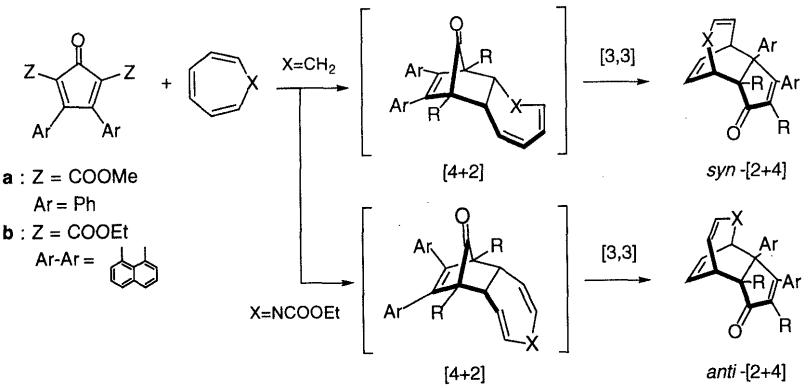

Chart 1

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structures (**3** and **6**) are depicted in Fig. 1.

The reaction barriers ($\Delta H_f^{TS} - \Delta H_f^{GS}$) of the [3,3]-sigmatropic rearrangement of DA cycloadduct at several levels were compared with those of the decarbonylation reaction of norbornen-7-one. The PM3[4] reaction barrier of [3,3]-sigmatropic rearrangement is higher than that of decarbonylation. The *ab initio* calculations at the 3-21G and 6-31G* levels also predicted that the [3,3]-sigmatropic rearrangement is unfavorable. Taking into consideration that the two pericyclic reactions involve oxygen and are of different types, MP2 level calculations are necessary for reliable prediction.[5] The MP2/6-31G* single point calculation of the 3-21G energies predicted that the reaction barrier of the [3,3]-sigmatropic rearrangement is lower than that of the decarbonylation by 3.9 kcal/mol. The MP2/6-31G* calculation showed the barrier of the [3,3]-sigmatropic rearrangement is 4.6 kcal/mol lower than that of the decarbonylation, supporting the relative

Table 1a. Energetics of Reactants and Transition States for the [3,3]-Sigmatropic Rearrangement of **3** and Decarbonylation of Norbornen-7-one

Geometry	Method	ΔH_f[a]	E[b]
[3,3]-Sigmatropic Rearrangement			
GS	PM3	14.6	
	RHF/3-21G		−419.0946
	RHF/6-31G*		−421.4344
	MP2/3-21G		−420.0175
	MP2/6-31G*//RHF/3-21G		−422.7561
	MP2/6-31G*//RHF/6-31G*		−422.7557
	MP2/6-31G*		−422.7599
TS	PM3	64.7	
	RHF/3-21G		−419.0132
	RHF/6-31G*		−421.3510
	MP2/3-21G		−419.9653
	MP2/6-31G*//RHF/3-21G		−422.7098
	MP2/6-31G*//RHF/6-31G*		−422.7098
	MP2/6-31G*		−422.7136
Decarbonylation			
GS	PM3	−5.9	
	RHF/3-21G		−342.6435
	RHF/6-31G*		−344.5570
	MP2/3-21G		−343.3882
	MP2/6-31G*//RHF/3-21G		−345.6258
	MP2/6-31G*//RHF/6-31G*		−345.6254
	MP2/6-31G*		−345.6288
TS	PM3	35.0	
	RHF/3-21G		−342.5719
	RHF/6-31G*		−344.4835
	MP2/3-21G		−343.3421
	MP2/6-31G*//RHF/3-21G		−345.5733
	MP2/6-31G*//RHF/6-31G*		−345.5729
	MP2/6-31G*		−345.5753

a) kcal/mol. *b*) Hartree.

Table 1b. Reaction Barriers for the [3,3]-Sigmatropic Rearrangement of **3** and Decarbonylation of Norbornen-7-one

Geometry	Method	$\Delta\Delta H_f$[a]	ΔE[a]
[3,3]-Sigmatropic Rearrangement			
GS→TS	PM3	50.1	
	RHF/3-21G		51.0
	RHF/6-31G*		52.3
	MP2/3-21G		32.7
	MP2/6-31G*//RHF/3-21G		29.0
	MP2/6-31G*//RHF/6-31G*		28.8
	MP2/6-31G*		29.0
Decarbonylation			
GS→TS	PM3	40.9	
	RHF/3-21G		44.9
	RHF/6-31G*		46.1
	MP2/3-21G		28.9
	MP2/6-31G*//RHF/3-21G		32.9
	MP2/6-31G*//RHF/6-31G*		33.0
	MP2/6-31G*		33.6

a) kcal/mol.

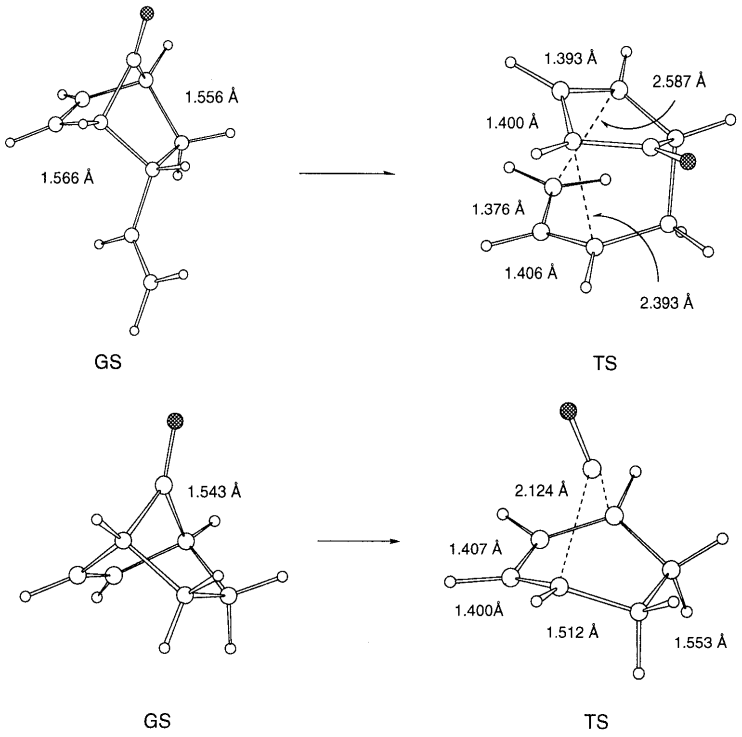

Fig. 1. The MP2/6-31G* GS and TS Structures for the [3,3]-Sigmatropic Rearrangement and Decarbonylation

reactivity at the MP2/6-31G*//RHF/3-21G single point level.

Based on the reactivity prediction by the MP2 calculation data, the pericyclic reactions of **1a** with some 1,3-alkadienes were investigated.

Cycloaddition of Cyclopentadienones with 1,3-Alkadienes Heating of a solution of 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (**1a**) and ethyl sorbate (**2a**) in benzene for 6 h gave the 1 : 1 adduct (**3aa**) in 78% yield. The infrared (IR) absorption spectrum of **3aa** exhibited a strained carbonyl band at 1788 cm^{-1}. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **3aa** showed that the methyl protons resonated at 1.29 ppm and the olefinic protons of the acrylic acid moiety appeared at 6.21 ppm, indicating that the propenyl moiety of the dienophile was attacked by the diene. The carbon nuclear magnetic resonance (^{13}C-NMR) spectral data also supported this assignment. Inspection of the ^{1}H detected heteronuclear multiple bond connectivity (HMBC) spectrum suggested that the cycloadduct is the *endo* one,[6] and this was later established by single-crystal X-ray analysis. Sorbic acid (**2b**) showed similar cycloaddition behavior.

The cycloaddition behavior of ethyl 5-phenyl-2,4-pentadienoate (**2d**) is different from that observed in sorbic acid derivatives. The acrylic acid moiety reacted with **1a** to give the *endo* DA adduct, in which the ethoxycarbonyl group is oriented toward the *endo* site and the styrene moiety toward the *exo* site, as confirmed by the X-ray analysis. 2,4-Hexadiene (**2c**) cycloadded to **1a** to give the DA adduct (**3ac**).

In the cycloaddition of the 2,5-bis(ethoxycarbonyl)acecyclone derivative (**1b**) with **2a**, the primary cycloadduct could not be isolated but the [3,3]-sigmatropic rearrangement product (**6ba**) was obtained.

Thermal Treatment of the DA Adducts of Cyclopentadienones and 1,3-Alkadienes Heating of **3aa** at 170 °C without solvent caused decarbonylation to give **5aa**. The ^{1}H- and ^{13}C-NMR spectra of **5aa** did not show any signals attributable to olefinic protons and carbons, suggesting the occurrence of intramolecular cycloaddition or dimerization of **4aa**. Inspection of the mass spectrum rules out the possibility of the dimeric compound (**7**). Comparison of the ^{1}H-NMR spectral data with those of structurally similar compounds[7] indicates the formation of the DDA adduct (**5aa**) having a cyclopropane ring. The methine proton signals appeared at higher fields characteristic of a cyclopropane skeleton. Similarly, heating of the DA adduct (**3ab**) of sorbic acid afforded the corresponding DDA adduct (**5ab**). Heating of the DA

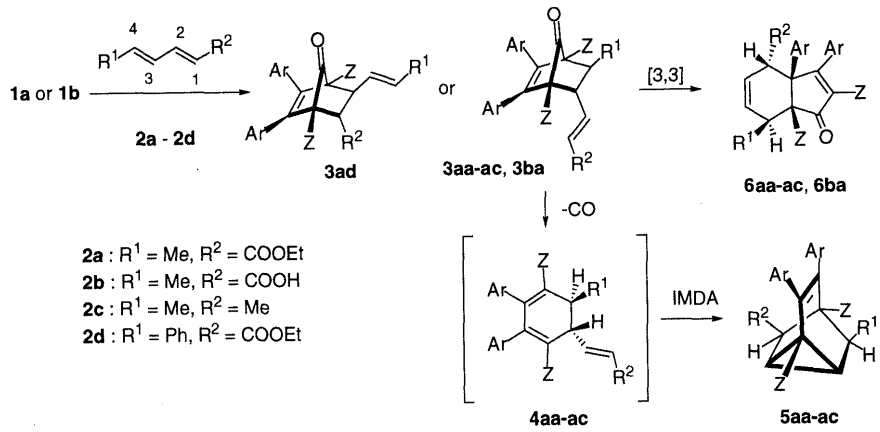

Chart 3

Table 2. Reaction Conditions and Products for DA Reactions of **1** with **2** and Thermal Treatment of the Cycloadducts (**3**)

Substrate	Solvent	Temp. (°C)	Time (h)	Yield(%) of products		
				DA	[3,3]	DDA
1a+**2a**	Benzene	Reflux	6	85 (**3aa**)		
3aa	Toluene	Reflux	24		33 (**6aa**)	
	None	170	8			64(**5aa**)
	o-Dichlorobenzene	120	24		68.5	31.5[a]
	o-Dichlorobenzene	130	18		47.6	52.4[b]
	o-Dichlorobenzene	150	12		32.3	67.7[c]
	o-Dichlorobenzene	170	10		5.9	94.1[d]
1a+**2b**	Benzene	Reflux	48	90(**3ab**)		
3ab	Chlorobenzene	110	18		43(**6ab**)	
1a+**2c**	Benzene	Reflux	12	76(**3ac**)		
3ac	*o*-Dichlorobenzene	140	72		46(**6ac**)	
	None	210	48			77(**5ac**)
1a+**2d**	Benzene	Reflux	6	82(**3ad**)		
1b+**2a**	Benzene	50	72		53(**6ba**)	

a) [3,3] : DDA = 1 : 0.46. *b*) [3,3] : DDA = 1 : 1.1. *c*) [3,3] : DDA = 1 : 2.1. *d*) [3,3] : DDA = 1 : 16.

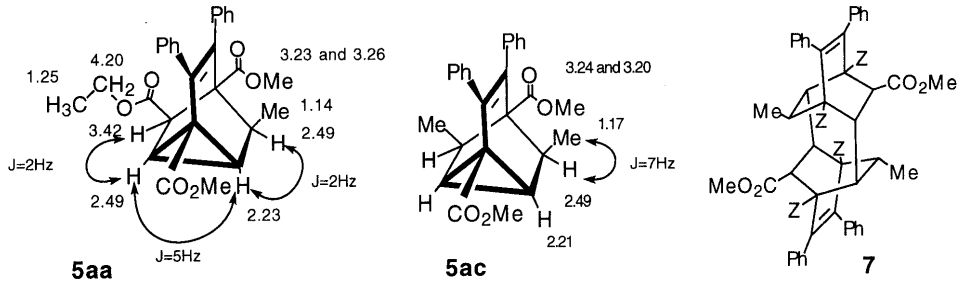

Fig. 2. 500 MHz ^{1}H-NMR Chemical Shifts (δ) of DDA Adducts (**5aa** and **5ac**)

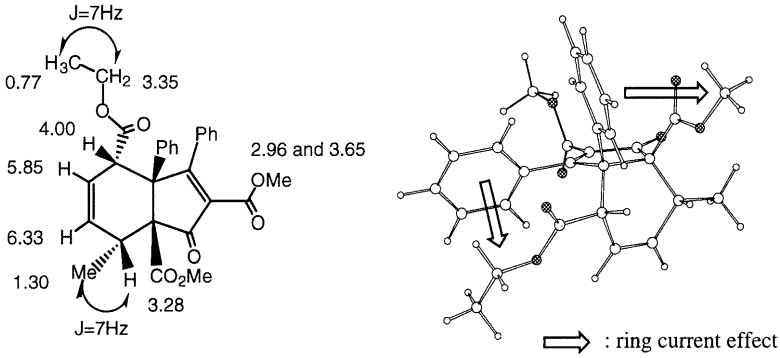

Fig. 3. 500 MHz ^{1}H-NMR Chemical Shifts (δ) and PM3-Optimized Structure of [3,3]-Sigmatropic Rearrangement Product (**6aa**)

adduct (**3ac**) of 2,4-hexadiene at 210 °C for 48 h afforded the corresponding DDA adduct (**5ac**) in 77% yield.

When the reaction was carried out under milder reaction conditions, the presence of another product was recognized by thin layer analysis and ^{1}H-NMR spectroscopy of the crude product (see Table 2). In the case of **3aa**, lowering the reaction temperature to 110 °C gave pale yellow crystals (**6aa**). The mass spectrum (MS) suggested the 1 : 1 adduct. The UV spectrum of **6aa** exhibited a visible absorption band at 372.8 nm, attributable to the n–π^* absorption of the 3-phenylcyclopentenone moiety. The IR spectrum also supported the presence of the enone structure. The ^{1}H- and ^{13}C-NMR spectra suggested that **6aa** is the [3,3]-sigmatropic rearrangement product of **3aa**. The phenyl and methoxycarbonyl groups at the ring juncture are *cis*-oriented, as determined on the basis of the high-field shift of the methoxy group (from 3.6 ppm in **3aa** to 2.96 ppm in **6aa**) due to the phenyl ring current effect. Inspection of a molecular model of the rearrangement product (**6aa**) indicated that the high-field shift of the methylene protons (3.4 ppm) should have arisen from the structure depicted in Fig. 3. The nuclear Overhauser and exchange spectroscopy (NOESY) spectrum of **6aa** showed a correlation between the two methine protons, indicating the spatial arrangement of the methine protons to be *cis*. The structures of **5ab, ac** were determined based on the similar evidence.

Single-crystal X-Ray Analyses of the DA Cycloadducts (3ab, 3ad) In order to establish the stereochemistry of the cycloadducts and to obtain information about the relationship between the stereochemistry and the reaction behavior of the DA cycloadducts, single-crystal X-ray analyses of **3ab** and **3ad** were performed. The crystal and analysis data are summarized in Table 3. Computer-generated drawings[8] of the molecules are depicted in Figs. 4 and 5.

Table 3. Crystal Data and Intensity Measurements for **3ab** and **3ad**

	3ab	**3ad**
Formula	$C_{27}H_{23}O_7$	$C_{34}H_{30}O_7$
mp (°C)	208—210	185—186
Crystal System	Triclinic	Monoclinic
Lattice Parameters		
a (Å)	10.571 (6)	10.559 (2)
b (Å)	12.646 (3)	10.741 (2)
c (Å)	10.139 (2)	25.010 (1)
α (°)	108.93 (1)	
β (°)	100.90 (3)	91.23 (1)
γ (°)	87.62 (3)	
V (Å^3)	1258.7 (8)	2835.8 (6)
Space Group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)
Z	2	4
D_{calc} (g/cm^3)	1.212	1.290
D_{exptl} (g/cm^3)	1.218	1.287
Solvent	EtOH	Xylene
Radiation	Mo K_α (λ=0.71069 Å)	
Scan range, deg	$2\theta < 55.0°$	
Unique data collected	6075	7220
Unique data used ($I > 3.00\sigma(I)$)	4092	3070
R	0.074	0.055
R_w	0.079	0.033

As shown in Figs. 4 and 5, the newly created bonds are found to be considerably elongated. This is especially notable in the latter case, where the bond lengths are 1.592(4) and 1.589(4) Å, respectively. These bond elongations could not be reproduced by molecular mechanics calculations (SYBYL[9a] and MM2[9b]). The semi-empirical SCF methods[3] showed moderate bond elongations, indicating that through-bond interactions[10] are operative between the π systems attached to the σ bond in question, and this is enhanced by the steric repulsions between

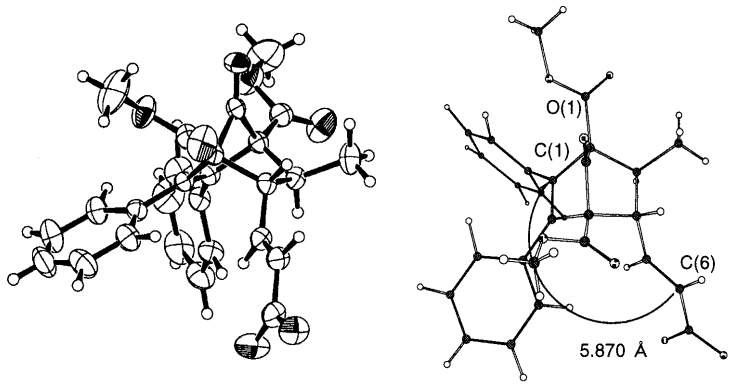

Fig. 4. X-Ray Crystal Structure of **3ab**

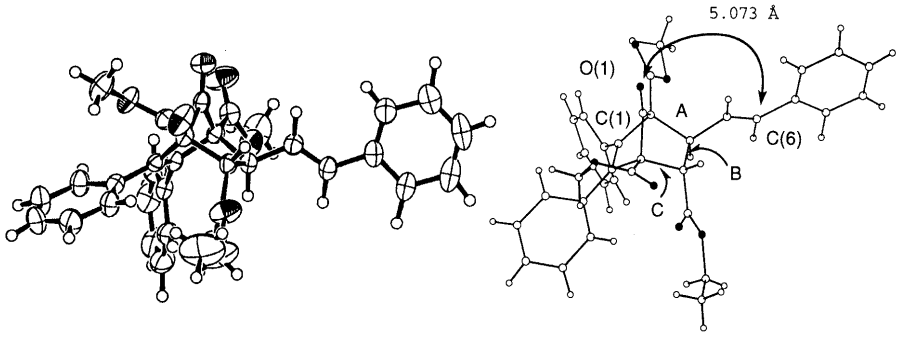

Fig. 5. X-Ray Crystal Structure of **3ad**

Table 4. Selected Bond Lengths of **3ad** Derived from X-Ray, MO and MM Calculations

	A (Å)	B (Å)	C (Å)
X-ray	1.592 (4)	1.566 (5)	1.589 (4)
PM3	1.565	1.569	1.566
AM1	1.564	1.564	1.562
MNDO	1.588	1.585	1.589
SYBYL	1.554	1.571	1.556
MM2[a)]	1.548	1.561	1.553

a) Parent molecule.

the substituents.[11)]

Discussion

The observed site-selectivity for the cycloaddition of **1a** with sorbic acid (**2b**) or ethyl sorbate (**2a**) can be explained in terms of frontier molecular orbital (FMO) theory.[12)] The reactions are inverse-type cycloadditions,[13)] in which the interaction between the LUMO of **1a** and the HOMO of **2a** is predominant. The sum (1.007) of the HOMO coefficients of the adjacent olefinic C3 and C4 carbons is larger than that (0.857) for C1 and C2, indicating that the propene moiety reacts with **1a**. The FMO prediction is in accordance with the observed site selectivity.

In the reaction with the ethyl 5-phenyl-2,4-pentadienoate (**2d**), the formation of the DA adduct is entirely inconsistent with the simple FMO prediction, which is that the reaction site should be the styrene moiety. Consideration of the next HOMO (NHOMO) rationalizes the experimental result. The NHOMO and HOMO energy levels of sorbic acid are -11.87 and -9.62, respectively. The replacement of the methyl group by the phenyl group raises the NHOMO and HOMO energy levels to -10.61 and -9.04, respectively, wherein the contribution of the NHOMO coefficients of the acrylic moiety is important for stabilization of the transition state (TS). The perturbation equation calculation involving the HOMO and NHOMO supports this assumption.[14a)] The calculation[14b)] of the reaction indicated that the stabilization energy for attack at the site of C_1 and C_2 is 1.42×10^{-2} eV lower than that at C_3 and C_4, whereas in the interaction between the LUMO of **1a** and the NHOMO of **2d**, the stabilization energy for attack at the site of C_3 and C_4 is 1.94×10^{-2} eV, less than that at C_1 and C_2.

Both *endo* and *exo* DA cycloadducts have a 1,5-diene (dienone) system available for [3,3]-sigmatropic rearrangement. However, the [3,3]-sigmatropic rearrangement was observed only in the *endo* cycloadducts. The *exo* cycloadduct gave the retro DA reaction product on heating.

In the crystal structure of the *endo* adduct **3ab**, the C1–C6 distance is 5.870 Å. The O1–C6 atomic distance of the *exo* adduct **3ad** is 5.073 Å, which is shorter than that of **3ab**. Without consideration of the steric interferences, the transformations from the *endo* and *exo* ground-state (GS) geometries to the corresponding TS seem not to be very difficult. In order to find the reaction barriers for both rearrangements, PM3 calculations on the parent adducts were carried out. The reaction barriers calculated by PM3 are included in Fig. 7. The reaction barrier in the [3,3]-sigmatropic rearrangement of the *exo* adduct is 6.0 kcal/mol higher than that of the *endo* adduct, indicating that the *exo* cycloadduct does not readily undergo [3,3]-sigmatropic rearrangement to give the [6+4]π

Table 5. FMO Energy Levels and Coefficients of **1a**, **2a** and **2d** Calculated by the PM3 Method

	1a			**2a**		**2d**		
Orbital levels								
	−10.46 (HOMO)	−1.72 (LUMO)		−9.621 (HOMO)	−0.671 (LUMO)	−10.61 (NHOMO)	−9.04 (HOMO)	−0.98 (LUMO)
Coefficients								
C_1 (C_4)	0.417	−0.460	C_1	0.530	0.476	0.450	−0.385	−0.406
C_2 (C_3)	−0.428	−0.333	C_2	0.327	−0.514	0.401	−0.196	0.375
			C_3	−0.482	−0.296	−0.086	0.449	0.372
			C_4	−0.525	0.494	−0.312	0.376	−0.438

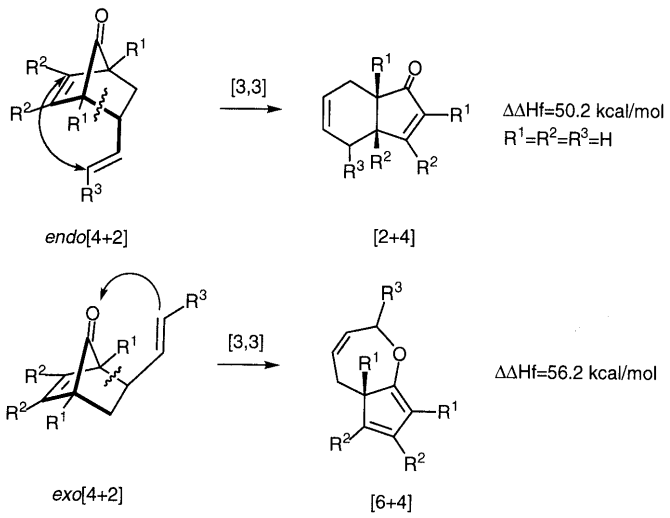

Fig. 6. PM3-Calculated Reaction Barriers for the Possible Reaction Pathways

cycloadduct.

As stated above, the rearrangements of the *endo* cycloadducts of 1,3-alkadienes required more severe reaction conditions than those for conjugated cyclopolyenes. The difference in rearrangement reactivity of the *endo* cycloadducts of 1,3-alkadiene from those of cyclopolyenes is attributable to the difference in their ground-state geometries. Inspection of the PM3 fully-optimized GS geometry of the *endo* [4+2]π cycloadducts of unsubstituted cyclopentadienone and cycloheptatriene indicates that the atomic distance for the interaction of the [3,3]-sigmatropic rearrangement is 3.780 Å, which corresponds to the initial stage of Cope rearrangements.[15]

The facile rearrangement of the DA adduct (**3ba**) of **1b** and **2a** can be accounted for in terms of the release of strain energy[1b] of the acenaphthylene-condensed norbornen-7-one moiety and the small steric crowding in the formation of the cyclic transition state compared with the case of **3aa**.

The formation reaction of the DDA adduct having a cyclopropane ring from 1,3-alkadienes is interesting. The DDA adducts are thermally stable in spite of the sizable strain energy (>50 kcal/mol).[16] The strain of the cyclopropane ring formation seems to affect the reaction barrier of the DDA adduct formation, which is calculated to be 12 kcal/mol higher than the value derived from the pericyclic reaction of cyclopentadienone with 1,5-hexadiene.

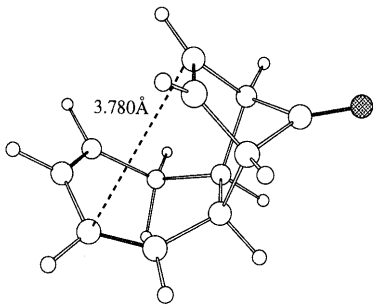

Fig. 7. PM3-Optimized Structure of *endo* [4+2]π Cycloadduct of Cyclopentadienone and Cycloheptatriene

In conclusion, the course of the sequential pericyclic reaction of cyclopentadienones with acyclic conjugated alkadienes depends on the reaction temperature. Pyrolysis of the DA adduct at a higher temperature gave the DDA cycloadduct having a cyclopropane ring, whereas thermal treatment at a lower temperature caused [3,3]-sigmatropic rearrangement to give the 3a,4,7,7a-tetrahydroinden-1-one derivative.

Experimental

Melting points were measured without correction. The IR spectra were taken with a Hitachi 270-30 spectrophotometer. High-resolution mass spectra (HRMS) were taken with a JEOL JMS-DX-303HF spectrometer. ^{1}H-NMR and ^{13}C-NMR spectra were taken with JEOL JNM-EX-270 (270 MHz), GX-400 (400 MHz) and JNM-A-500 (500 MHz) spectrometers for *ca.* 10% solution with tetramethylsilane (TMS) as an internal standard; chemical shifts are expressed as δ values and the coupling constants (J) are expressed in Hz.

Molecular Orbital Calculation Semi-empirical SCF MO calculations[3] were run through the ANCHOR II (Assistance of New Chemistry for Original Research, Fujitsu Ltd.) interface using MOPAC6.02c on a Fujitsu S4/2 engineering work station (EWS). The *ab initio* computations,[3] running on an S4/10 EWS or a Convex Exemplar SPP-1000 parallel processing computer were carried out using 3-21G and 6-31G basis sets and the gradient technique with optimization of all variables. The stationary points calculated for the transition states of the decarboxylation and Cope reactions by the PM3 method were used as starting geometries. We characterized the stationary point for the synchronous mechanism as a true transition state having a single negative Hessian eigenvalue. The calculation data are available upon request by E-mail (E-mail address: harano@gpo.kumamoto-u.ac.jp).

Materials 2,5-Bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone[17] (**1a**) and 2-oxo-1,3-bis(ethoxycarbonyl)-2*H*-cyclopent[a]acenaphthylene[18] (**1b**) were prepared according to the reported methods.

Cycloadditions of 1 with Some Dienophiles (General Procedure) A mixture of **1** (0.5 g, 1.44 mmol) in an excess dienophiles (7.2—14.4 mmol) in benzene (1 ml) was heated at 75—80 °C until the red color disappeared. The solvent was removed under reduced pressure. The residual oil was treated with methanol to give a solid, which was collected and recrystallized from EtOH to give the *endo* DA adduct as colorless needles.

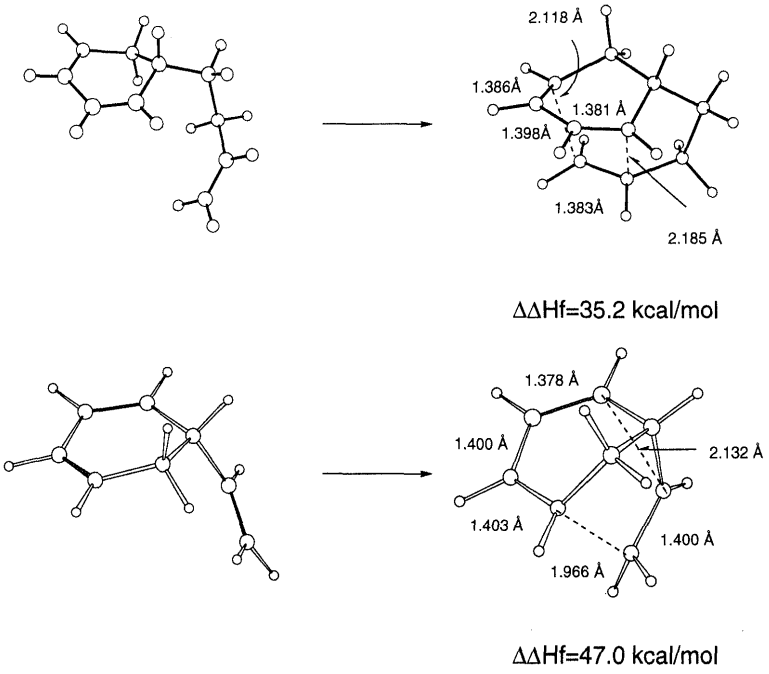

Fig. 8. PM3-Optimized Transition Structures and Energies for Model IMDA Reactions

The following compounds were obtained by essentially the same procedure as above.

3aa: Colorless prisms, mp 157—160 °C (from EtOH). IR (KBr): 1788 (bridge >C=O), 1738, 1712 (ester >C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.29 (6H, m, methyl × 2), 2.29 (1H, dd, J=7, 5 Hz, methine-*endo*), 3.18—3.16 (1H, m, methine-*exo*), 3.58 (3H, s, –OMe), 3.61 (3H, s, –OMe), 4.21 (2H, m, methylene), 6.21 (1H, d, J=15 Hz, –CH=CH–COOEt), 6.88 (1H, dd, J=15, 9 Hz, –CH=CH–COOEt), 7.35—7.02 (10H, m, aromatic H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 14.3 and 16.8 (methyl), 41.1 and 49.7 (methine), 51.9 and 52.4 (–OMe), 60.6 (methylene), 67.9 and 68.2 (quaternary carbon), 124.5 (olefin), 127.3, 127.6, 127.7, 128.0, 128.1, 128.2, 128.4, 128.7, 129.1 and 129.9 (aromatic CH), 132.8, 132.9, 137.6 and 140.5 (quaternary carbon), 145.7 (olefin), 165.8, 166.5 and 167.3 (ester >C=O), 190.0 (bridge >C=O). MS m/z: 488 (M^+), 460 ($M^+ - CO$). *Anal.* Calcd for $C_{29}H_{28}O_7$: C, 5.78; H, 71.30. Found:C, 5.83; H, 70.77.

3ab: Colorless prisms, mp 208—210 °C (from EtOH). IR (KBr): 1794 (bridge >C=O), 1734 (ester >C=O) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.31 (3H, d, J=7 Hz, methyl), 2.33 (1H, dd, J=12, 7 Hz, methine-*endo*), 3.23 (1H, dd, J=9, 4 Hz, methine-*exo*), 3.58 and 3.62 (6H, each s, –OMe × 2), 6.23 (1H, d, J=15 Hz, –CH=CH–COOH), 7.03 (1H, dd, J=15, 9 Hz, –CH=CH–COOH), 6.92—7.30 (10H, m, aromatic H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 16.8 (methyl), 41.1 and 49.7 (methine), 51.9 and 52.4 (–OMe), 67.9 and 68.1 (quaternary carbon), 123.7 (olefin), 128.0, 128.1, 128.6 and 128.7 (aromatic CH), 132.7, 132.8, 137.5 and 140.6 (quaternary carbon), 148.5 (olefin), 166.4, 167.1 and 170.9 (ester >C=O), 189.7 (bridge >C=O). MS m/z: 460 (M^+), 432 ($M^+ - CO$).

3ac: Colorless prisms, mp 79—82 °C (from MeOH). IR (KBr): 1790 (bridge >C=O), 1736 (ester >C=O) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.25 (3H, d, J=7 Hz, methyl), 1.77 (3H, d, J=7 Hz, methyl), 2.16 (1H, dd, J=12, 6 Hz, methine), 2.99 (1H, dd, J=12, 6 Hz, methine), 3.55, 3.62 (6H, each s, –OMe × 2), 5.43 (1H, dd, J=15, 9 Hz, –CH=CH–Me), 5.91 (1H, dd, J=15, 7 Hz, –CH=CH–Me), 7.00—7.29 (10H, m, aromatic H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 16.6 (methyl), 18.0 (methyl), 41.6 (methine), 49.9 (methine), 51.7 and 52.1 (–OMe), 68.1 and 68.8 (quaternary carbon), 127.6, 127.9, 128.0, 128.2, 128.3, 128.5, 128.6, 128.7, 128.8 and 128.9 (aromatic CH), 128.9 and 129.5 (olefin), 133.5, 133.6, 137.9 and 139.6 (quaternary carbon), 166.9 and 167.9 (ester >C=O), 191.6 (bridge >C=O). MS m/z: 430 (M^+). *Anal.* Calcd for $C_{27}H_{26}O_5$: C, 75.33; H, 6.09. Found: C, 75.45; H, 6.10.

3ad: Colorless prisms, mp 185—186 °C (from xylene). IR (KBr): 1800 (bridge >C=O), 1724 (ester >C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.19 (3H, t, J=7 Hz, methyl), 3.49 and 3.69 (6H, each s, –OMe × 2), 3.67 (1H, dd, J=9, 5 Hz, methine-*exo*), 3.76 (1H, d, J=5 Hz, methine-*endo*), 4.06—4.20 (2H, m, methylene), 6.13 (1H, dd, J=15, 9 Hz, –CH=CH–Ph), 6.64 (1H, d, J=15 Hz, –CH=CH–Ph), 7.01—7.33 (15H, m, aromatic H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 13.9 (methyl), 47.0 (methine), 49.3 (methine), 51.8 and 52.4 (–OMe), 61.8 (methylene), 67.6 and 68.1 (quaternary carbon), 123.6 (olefin), 125.7, 126.4, 127.5, 127.7, 127.9, 128.3, 128.4, and 128.6 (aromatic CH), 128.8 (olefin), 129.9, 132.9, 136.4, 137.6 and 140.2 (quaternary carbon), 165.9, 166.6 and 170.9 (ester >C=O), 188.9 (bridge >C=O). MS m/z: 550 (M^+).

Thermolysis of the [4+2]π Cycloadduct (General Procedure). Formation of DDA Adduct The DA adduct (1.0 g) was heated at 170 °C without solvent to give an oil with evolution of CO gas. The resulting oil was purified by chromatography on silica gel with AcOEt–benzene (1 : 20) to give the DDA adduct as colorless prisms.

The following compounds were obtained by essentially the same procedure as above.

5aa: Colorless needles, mp 102 °C (from EtOH). IR (KBr): 1734 (ester >C=O) cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 1.14 (3H, d, J=7 Hz, methyl), 1.25 (3H, t, J=6 Hz, methyl), 2.23 (1H, dd, J=5, 2 Hz, methine), 2.49 (2H, m, methine × 2), 3.23 and 3.26 (6H, each s, –OMe × 2), 3.42 (1H, d, J=2 Hz, methine), 4.20 (2H, q, J=7 Hz, methylene), 6.96—7.08 (10H, m, aromatic H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 13.0 (methyl), 14.6 (methyl), 28.7 (methine), 30.3 (methine), 33.1 (quaternary carbon), 39.1 (methine), 47.7 (methine), 51.8 and 52.1 (–OMe), 58.2 (quaternary carbon), 60.9 (methylene), 126.2, 126.3, 127.3, 127.6, 128.3, 128.7, 128.9, 129.0, 129.3 and 130.1 (aromatic CH), 134.3, 139.2 and 139.9 (quaternary carbon), 170.9, 171.6 and 172.4 (>C=O). MS m/z: 488 (M^+), 387 ($M^+ - CO_2Et$). *Anal.* Calcd for $C_{28}H_{28}O_6$: C, 73.03; H, 6.13. Found: C, 73.26; H, 6.16.

5ac: Colorless prisms. mp 135—136 °C (from EtOH–acetone). IR (KBr): 1726 (ester >C=O) cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 1.17 (6H, d, J=7 Hz, methyl), 2.11 (2H, s, methine), 2.47 (2H, q, J=7 Hz, >CH–Me), 3.20 and 3.24 (6H, each s, –OMe × 2), 6.81—7.26 (10H, m, aromatic H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 13.4 (methyl), 31.4 and 37.8 (methine), 32.1 (quaternary carbon), 51.0 and 51.6 (–OMe), 58.7 (quaternary carbon), 125.8, 125.9, 127.2, 127.3, 129.0 and 129.1 (aromatic CH), 132.9, 139.4 and 139.7 (quaternary carbon), 171.9 and 173.6 (>C=O). MS m/z: 402 (M^+), 343 ($M^+ - CO_2Me$). *Anal.* Calcd for $C_{26}H_{26}O_4$: C, 77.59; H, 6.51. Found: C, 77.68; H, 6.55.

Cope Rearrangement of [4+2]π Cycloadduct (General Procedure) A solution of DA adduct (0.50 g) in toluene (2 ml) was refluxed for 24 h. The solvent was evaporated under reduced pressure. The residual oil was purified by chromatography on silica gel using AcOEt–benzene (1 : 20) as an eluent to give the Cope rearrangement product.

The following compounds were obtained by essentially the same procedure as above.

6aa: Pale yellow prisms, mp 110—113 °C (from EtOH). IR (KBr): 1738 (>C=O)cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.77 (3H, t, J=7 Hz, methyl), 1.30 (3H, d, J=7 Hz, methyl), 2.96 (3H, s, –OMe), 3.28 (1H, m, methine), 3.35 (2H, q, J=7 Hz, methylene), 3.65 (3H, s, –OMe), 4.00 (1H, br s, methine), 5.85 (1H, ddd, J=13, 6, 3 Hz, –(CO)CH–CH=CH–CH(Me)–), 6.33 (1H, ddd, J=13, 7, 4 Hz, –(CO)CH–CH=CH–CH(Me)–), 7.36—7.14 (10H, m, aromatic H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 13.0 (methyl), 15.3 (methyl), 37.0 (methine), 44.5 (methine), 52.1 and 51.4 (–OMe), 60.6 (methylene), 68.3 and 74.0 (quaternary carbon), 126.7 (olefin), 126.8, 127.7, 127.8, 128.2, 129.1, 130.1, 130.4 and 133.6 (aromatic CH), 133.6, 136.3, 140.9 and 163.7 (quaternary carbon), 136.3 (olefin), 168.9, 169.9, 174.2 and 196.5 (>C=O). MS m/z: 488 (M^+). HRMS Calcd for $C_{29}H_{28}O_7$ (M^+): 488.1858. Found: 488.1835.

6ab: Pale yellow needles, mp 158—160 °C (from EtOH–toluene). IR (KBr): 1738 (>C=O)cm^{-1}. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.31 (3H, d, J=7 Hz, methyl), 2.96 (3H, s, –OMe), 3.28 (1H, m, methine), 3.65 (3H, s, –OMe), 3.98 (1H, s, methine), 5.86 (1H, ddd, J=13, 6, 3 Hz, –(CO)CH–CH=CH–CH(Me)–), 6.34 (1H, ddd, J=13, 7, 4 Hz, –(CO)CH–CH=CH–CH(Me)–), 7.36—7.14 (10H, m, aromatic H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 15.3 (methyl), 37.0 (methine), 44.5 (methine), 52.1 and 51.4 (–OMe), 68.3 and 74.0 (quaternary carbon), 126.7 (olefin), 126.8, 127.7, 127.8, 128.2, 129.1, 130.1, 130.4 and 133.6 (aromatic CH), 133.6, 136.3, 140.9 and 163.7 (quaternary carbon), 136.3 (olefin), 168.9, 169.0, 175.8 and 199.6 (>C=O). MS m/z: 488 (M^+). *Anal.* Calcd for $C_{27}H_{24}O_7$: C, 70.42; H, 5.25. Found: C, 70.40; H, 5.28.

6ac: Pale yellow prisms, mp 174—174.5 °C (from MeOH–AcOEt). IR (KBr): 1738 (>C=O)cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.58 (3H, d, J=7, methyl), 1.24 (3H, d, J=7 Hz, methyl), 2.95 (3H, s, –OMe), 3.26—3.25 (1H, m, methine), 3.35—3.44 (1H, m, methine), 3.66 (3H, s, –OMe), 5.61—5.58 (1H, m, –CH=CH–CH(Me)–C(Z)<), 5.78—5.75 (1H, m, –CH=CH–CH(Me)–C(Z)<), 7.40—7.07 (10H, m, aromatic H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 15.7 (methyl), 16.5 (methyl), 34.9 (methine), 37.3 (methine), 51.7 and 52.1 (–OMe), 68.8 and 74.5 (quaternary carbon), 127.9, 128.0, 128.6 and 129.9 (aromatic CH), 133.2 and 134.3 (olefin), 136.1, 137.0, 140.9 and 164.0 (quaternary carbon), 170.4, 175.6 and 197.2 (>C=O). MS m/z: 430 (M^+). *Anal.* Calcd for $C_{27}H_{26}O_5$: C, 75.33; H, 6.09. Found: C, 75.56; H, 6.25.

6ba: Yellow prisms, mp 122—123 °C (from EtOH–Acetone). IR (KBr): 1746, 1728 (>C=O)cm^{-1}. ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 0.39, 0.54 and 1.43 (9H, t, methyl×3), 1.77 (3H, d, J=7 Hz, methyl), 3.00—2.95 (1H, m, methylene), 3.22—3.27 (2H, m, methine and methylene), 3.48—3.50 (1H, m, methine), 3.75—3.80 and 3.54—3.61 (2H, m, methylene), 4.39—4.44 (2H, m, methylene), 5.89—5.92 (1H, m, –(CO)CH–CH=CH–CH(Me)–), 6.07—6.10 (1H, m, –(CO)CH–CH=CH–CH(Me)–), 7.56—7.80, 7.99 and 8.52 (6H, m, aromatic H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 13.0, 13.2, 14.3 and 15.7 (methyl), 35.1 and 54.3 (methine), 60.7, 61.0 and 61.1 (methylene), 66.1 and 69.4 (quaternary carbon), 124.9 (olefin), 121.6, 125.1, 126.1, 126.6, 128.3, 128.4, 130.4 and 132.3 (aromatic CH), 138.7 (olefin), 132.3, 139.8, 140.2 and 162.0 (quaternary carbon), 168.9, 170.6, 183.9 and 199.3 (>C=O). MS m/z: 488 (M^+). *Anal.* Calcd for $C_{29}H_{28}O_7$: C, 71.30; H, 5.78. Found: C, 71.19; H, 5.74.

X-Ray Crystallography *exo* [4+2]π Cycloadduct 3ab Single-crystals of the compound **3ab** were prepared by slow evaporation of an ethanol solution at room temperature. X-Ray measurements were performed with a Rigaku AFC7R four-circle autodiffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ=0.7107 Å) and a rotating anode generator. The unit-cell constants were determined from a least-squares procedure using the values of the Bragg angles of 25 reflections. The space group $P\bar{1}$(#2) was selected from the number of molecules per unit cell (Z=2) and was later confirmed in the course of the structure refinement. Intensity data were collected in the range of 2θ <55° using the ω–2θ scan technique. Three reflections were monitored after every measurement of 100 reflections. Of the 6075 independent reflections, 4092 were treated as observed (I>3.00 $\sigma(I)$). The intensities were corrected for Lorentz and polarization effects, but no correction was applied for absorption. The structures were solved by the direct method (SAPI91[19]). The non-hydrogen atoms were refined anisotropically and the hydrogen atoms of the three methyl groups were included but not refined. The final cycle of full-matrix least-square refinement converged with unweighted (R) and weighted agreement factors (R_w) of 0.074 and 0.079, respectively. The crystal data and X-ray experimental details are summarized in Table 3. All calculations were performed on a Silicone Graphics IRIS Indigo WS with the teXsan[20] Crystal Structure Analysis Package. Anisotropic thermal parameters of non-hydrogen atoms, atomic coordinates, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

***exo* [4+2]π Cycloadduct 3ad** The data collection, phasing, and refinement for **3ad** were carried out in almost the same manner as for **3ab** (Table 3).

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$$\Delta E_{\text{LUMO(1a)-HOMO(2d for C1 and C2)}} = 1.41 \times 10^{-2}\ \text{eV},$$

$$\Delta E_{\text{LUMO(1a)-HOMO(2d for C3 and C4)}} = 2.83 \times 10^{-2}\ \text{eV}.$$

$$\Delta E_{\text{LUMO(1a)-NHOMO(2d for C1 and C2)}} = 2.48 \times 10^{-2}\ \text{eV}.$$

$$\Delta E_{\text{LUMO(1a)-NHOMO(2d for C3 and C4)}} = 0.54 \times 10^{-2}\ \text{eV}.$$

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