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MO Analysis of Photocycloaddition Reactions of 2-Pyrones

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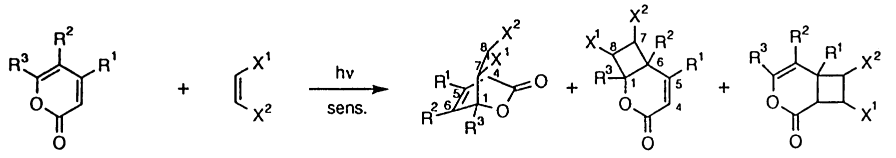
The skeleton of the 2-pyrones (**1**) is a simple one composed of 2,4-pentadien-5-olides, but has many possibilities for photocycloadditions. To elucidate the peri-, site-, and regioselective photoadditions of the triplet 2-pyrones with some ethylenes, the factors were analyzed by PM3-CI-UHF methods, etc. The regioselective [4+2]cycloadducts (**3**) and site-selective [2+2]cycloadducts (**4**) across the C_5–C_6 double bonds of the 2-pyrones with electron-deficient ethylenes were deduced to be formed by their preferable HSOMO–LUMO interactions and via more stable biradicals by the C_6–C_β bondings. On the other hand, the other kinds of regioselective [4+2] (**6**) and [2+2]adducts (**5**) across the C_3–C_4 double bonds of the 2-pyrones with an electron-donating ethylene were inferred to mainly come from LSOMO–HOMO interactions and via biradicals by C_3–C_β bondings. Selectivities between **3** and **4**, and **5** and **6** were also inferred to be caused by SOMOs of the biradicals.

2-Pyrone (**1**) is a simple 2,4-pentadien-5-olide and has an $\alpha,\beta:\gamma,\delta$-unsaturated carbonyl system. The cycloaddition reactivity of the photoexcited states of **1** is very interesting from the physical and chemical points of photoexcited states. The investigation of the photocycloadditions has not been extended beyond our reports.[1–3] In our previous paper, a variety of sensitized reactions of 2-pyrones with unsaturated compounds were mentioned.[4] Coldwell et al. successfully analyzed the regioselectivity of photo[2+2]cycloadditions of substituted phenanthrenes by calculation of the perturbation energies by means of the CNDO method.[5] Ramamurthy et al. also explained regioselective thiethane formation from photoexcited enethiones by a PMO model in conjunction with MINDO/3 calculations.[6] We now report a summary of the whole result concerning the photoadditions of **1** with ethylenes (**2**) including siteselective [2+2]cycloadditions and regioselective [4+2]cycloadditions, and the MO analysis by the use of PM3-CI-UHF[7] methods etc.

Table 1. Photocycloaddition Reactions of Substituted 2-Pyrones with Ethylenes in the Presence of Photosensitizers



1	**2**	**3**	**4**	**5**
R^1, R^2, R^3,	X^1, X^2	aez, agx	ah, bg	bi
a: H, CO_2Me, H	e: DMAD	ahx, ahn	bh, cf	chw
b: Me, CO_2Et,Me	f: COOCO	bfx, bgx	cg, ch	ci
c: Me, H, Me	h: H, CN	bhx, bhn	dh	di
d: OMe, H, Me	i: H, OEt	cfx, cf		
		cgx, dez		

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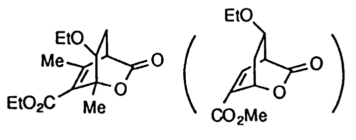


6 bi **7** ai

	2e	2f	2g	2h	2i
1a	**3aez**(50)[a)]	Dimer[b)]	**3agx**(50)[c)]	**3ahx**(12)[d)]+**3ahn**(17)[e)]+**4ah**(9)	(**7ai**(94))[f)]
1b	—	**3bfx**(54)	**3bgx**(59)[g)]+**4bg**(19)	**3bhx**(8)+**3bhn**(8)+**4bh**(61)	**5bi**(71)+**6bi**(9)
1c	—	**3cfx**(52)+**3cf**(12)[h)]+**4cf**(20)	**3cgx**(78)[g)]+**4cg**(12)	**4ch**(39)+**5chw**(3)[i)]	**5ci**(83)[j)]
1d	**3dez**(35)	No adduct	No addut[g)]	**4dh**(46)	**5di**(75)[j)]

( ): Product yield; —: No experiment. a) z means decarboxylation. b) Pyrone dimer. c) Y= p-$NO_2C_6H_4$. d) x means *exo*-[4+2]adduct. e) n means *endo*-[4+2]adduct. f) Thermal reaction. g) Y=H. h) bis-adduct by way of [4+2]addition. i) w means hydration. j) GC data.

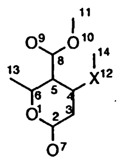
Results and Discussion

Summary of Photoadditions of 2-Pyrones. The results of photoadditions between 2-pyrones (**1**) and ethylenes (**2**) are summarized in Table 1.[1–4] The photoreactions were carried out in the presence of benzophenone as a sensitizer with a 400 W high-pressure mercury lamp. Table 1 shows that there were four kinds of primary photoadducts: **3**, **4**, **5**, and **6**, and the distribution was inferred to mainly depend on the electronic properties of the two substrates. Namely, the decrease in the electron-withdrawing property of the substituents on the two substrates, **1** and **2** (left to right, and high to low in Table 1), changed the product-distribution as follows:

$$\mathbf{3} \longrightarrow \mathbf{3}+\mathbf{4} \longrightarrow \mathbf{4} \longrightarrow \mathbf{4}+\mathbf{5},\ \mathbf{5}+\mathbf{6}\,(\text{minor}) \longrightarrow \mathbf{5} \qquad (1)$$

Those results are inferred to reflect the excited triplet properties of 2-pyrones in the photoadditions and properties of the intermediates.

Table 2. Optimized Geometries for the First Triplet Excited State of **1** by the PM3-UHF Calculation



	1a(So)	**1a**	**1b**	**1c**	**1d**
	A. Bond length/Å$^{a)}$				
O1–C2	1.397	1.384	1.380	1.381	1.378
C2–C3	1.461	1.475	1.472	1.474	1.475
C3–C4	1.349	1.478	1.486	1.483	1.491
C4–C5	1.443	1.386	1.404	1.388	1.404
C5–C6	1.367	1.437	1.442	1.437	1.427
C6–O1	1.343	1.352	1.358	1.360	1.363
C2–O7	1.208	1.229	1.228	1.230	1.230
C5–C8	1.478	1.502	1.507		
C8–O9	1.218	1.226	1.227		
C8–O10	1.368	1.359	1.360		
O10–C11	1.412	1.406	1.406		
C4–X12			1.499	1.497	1.348
C6–C13			1.509	1.504	1.505
C12–C14					1.404
	B. Angle (/°)				
O1–C2–C3	119.5	118.6	118.2	119.3	119.6
C2–C3–C4	119.5	119.0	119.2	119.3	117.9
C3–C4–C5	119.4	118.3	116.2	116.4	118.1
C4–C5–C6	119.0	120.0	121.0	122.3	120.6
C5–C6–O1	121.6	122.5	121.0	121.0	121.6
C6–O1–C2	121.0	121.7	122.5	121.6	122.1
O1–C2–O7	108.5	114.3	114.5	114.1	114.2
C4–C5–C8	122.1	121.5	120.8		
C5–C8–O9	126.4	125.8	126.1		
C5–C8–O10	114.7	113.0	113.0		
C8–C10–C11	118.4	125.1	125.2		
C3–C4–X12			117.7	120.3	113.5
C5–C6–C13			126.3	125.1	125.0
C4–O12–C14					123.6
	C. Dihedral angle/$^{\circ b)}$				
C3–C4–C5–C6	−0.1	0.2	7.2	0.0	0.1
C4–C5–C6–O1	0.0	0.1	3.8	0.0	0.1
C5–C6–O1–C2	−0.1	−0.1	−6.5	0.0	−0.1
C6–O1–C2–O7	179.9	179.8	178.6	180.0	179.9
C3–C4–C5–C8	179.9	181.2	185.6		
C4–C5–C8–O9	179.6	88.7	−93.8		
C4–C5–C8–O10	−0.4	−91.2	86.0		
C5–C8–O10–C11	180.0	179.8	−179.8		
C2–C3–C4–X12			164.9	180.0	179.7
C4–C5–C6–C13			182.0	180.0	180.0
C3–C4–O12–C14					180.0

a) X=C or O. b) For example, $C_3C_4C_5C_6$ means the dihedral angle between the plane of $C_3C_4C_5$ and $C_4C_5C_6$.

Triplets of 2-Pyrones and Factors of the Photocycloadditions. Table 2 shows optimized geometries for the first-triplet excited states of four 2-pyrones **1a**, **1b**, **1c**, and **1d** by PM3-CI-UHF calculations. The **1a** (So) in Table 2 means an optimized structure of the ground state of **1a** for a reference, and the calculated data are almost consistent with X-ray data of 2-pyrones.[8]

The geometries of four first-triplet 2-pyrones in Table 2 are also thought to be reasonable, respectively. Dihedral angles in **1a** and **1b** show that the methoxycarbonyl groups at the 5-positions are twisted with the pyrone rings. Figure 1 shows energies and coefficients of higher singly occupied molecular orbitals (HSOMO) and lower ones (LSOMO) of the triplet states by means of the UHF-CI method, and those of LUMO and HOMO of the ground states of three ethylenes, **2f**, **2h**, and **2i**, by means of the RHF-CI method. As the photoadditions were sensitized by some triplet sensitizers,[1–4] they were inferred to go through two-step radical paths, and that the first steps were mainly influenced by coefficients and energies of the two frontier orbitals, respectively.[5,9] The reasonable processes via radical intermediates (**8**, **9**) in Scheme 1 are inferred from the narrow gaps (ΔE) of the energies and the large coefficients (C_i, C_r) between two substrates in Fig. 1, and are quantitatively confirmed by large two-center frontier orbital interactions in Table 3. The interactions, $(C_iC_r)^2/\Delta\varepsilon$ (in γ^2/eV) have a tendency to be larger between C_6(**1**) and C_β(**2**), or C_3(**1**) and C_β(**2**) than others. In the concrete, with **2f** possessing two strong electron-withdrawing groups, the C_6(**1**)–C_β(**2f**) interactions between the HSOMO–LUMO are larger than the others, and with **2i** possessing an electron-donating group, the C_3–C_β interactions between the LSOMO–HOMO are far larger. In the case of **2h** having an electron-withdrawing group, the C_6(**1**, HSOMO)–C_β(**2**, LUMO) interactions are nearly equal to the C_3(LSOMO)–C_β(HOMO) interactions. They strongly support that

Table 3. Estimated Frontier Orbital Interactions Between **1** and **2** by the PM3-CI Calculation (γ^2/eV)

Position	**2f**		**2h**		**2i**	
	6-β	3-β	6-β	3-β	6-α	3-β
1a	0.064$^{a)}$	0.026$^{b)}$	0.060	0.039	0.048	0.064
1b	0.064	0.027	0.060	0.039	0.047	0.063
$(C_iC_r)^2/\Delta\varepsilon$ **1c**	0.068	0.025	0.060	0.057	0.047	0.056
1d	0.064	0.031	0.057	0.046	0.044	0.072

a) left: HSOMO (**1**)–LUMO (**2**) interaction. b) right: LSOMO (**1**)–HOMO (**2**) interaction.

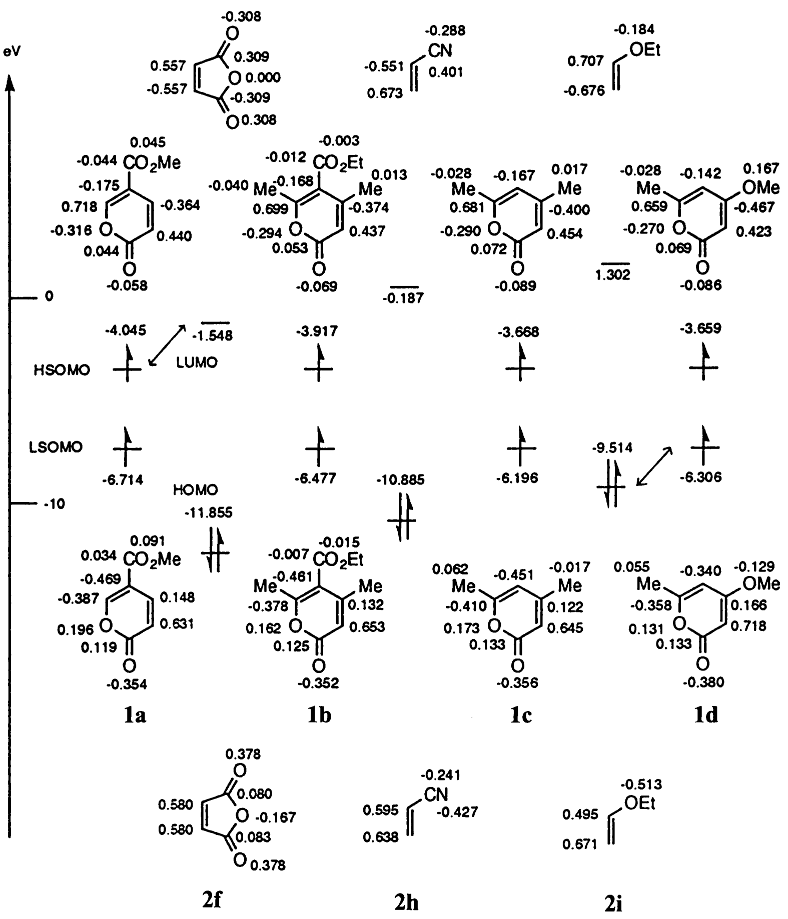
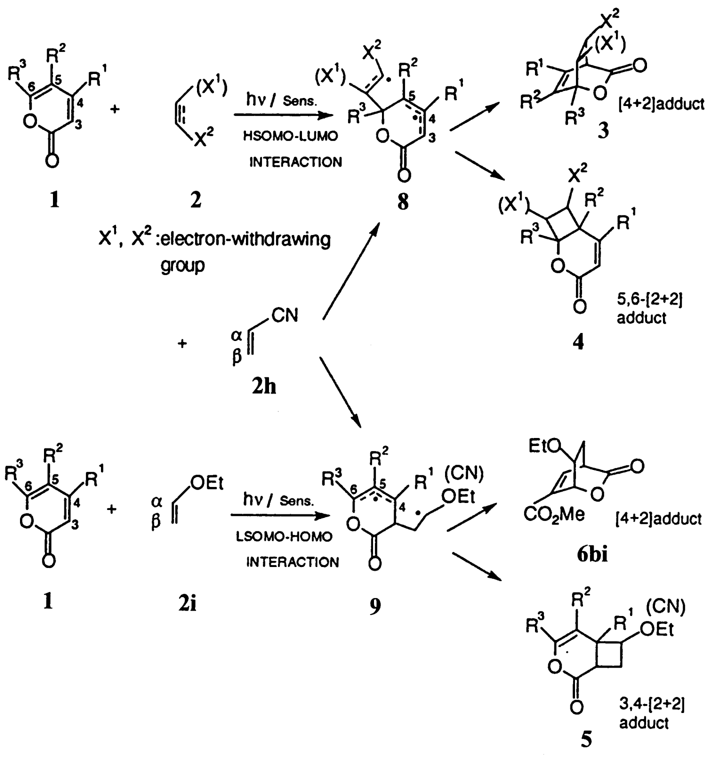


Fig. 1. Estimated energies and coefficients of triplet 2-pyrones and ground-state substituted ethylenes by means of PM3-CI methods.



Scheme 1.

Table 4. Estimated Energies and Coefficients of the First Triplets of 2-Pyrones, **1a** and **1b**

	1a			**1b**		
	PM3	AM1	MNDO	PM3	AM1	MNDO
HSOMO O_1	0.316	0.316	0.305	0.294	0.293	0.279
C_2	−0.044	−0.032	−0.072	−0.053	−0.035	−0.043
C_3	−0.440	−0.438	−0.461	−0.437	−0.416	−0.470
C_4	0.364	0.370	0.358	0.374	0.358	0.450
C_5	0.175	0.176	0.195	0.168	0.169	0.116
C_6	−0.718	−0.727	−0.725	−0.699	−0.709	−0.637
Energy/eV	−4.045	−3.959	−4.034	−3.917	−3.790	−4.170
LSOMO O_1	0.196	0.183	0.188	0.162	0.144	0.158
C_2	0.119	0.130	0.120	0.125	0.129	0.125
C_3	0.631	0.631	0.645	0.653	0.637	0.649
C_4	0.148	0.159	0.151	0.132	0.140	0.219
C_5	−0.469	−0.471	−0.478	−0.461	−0.469	−0.364
C_6	−0.387	−0.385	−0.406	−0.378	−0.361	−0.395
Energy/eV	−6.714	−6.835	−6.509	−6.477	−6.573	−6.421

Table 5. Estimated Energies and Coefficients of the First Triplets of 2-Pyrones, **1c** and **1d**

	1c			**1d**		
	PM3	AM1	MNDO	PM3	AM1	MNDO
HSOMO O_1	0.290	0.293	0.280	0.270	0.274	0.268
C_2	−0.072	−0.072	−0.061	−0.069	−0.066	−0.037
C_3	−0.454	−0.459	−0.506	−0.423	−0.426	−0.449
C_4	0.400	0.414	0.448	0.467	0.469	0.464
C_5	0.167	0.164	0.135	0.142	0.149	0.161
C_6	−0.681	−0.665	−0.633	−0.659	−0.651	−0.650
Energy/eV	−3.668	−3.561	−3.904	−3.659	−3.560	−3.758
LSOMO O_1	0.173	0.166	0.177	0.131	0.120	0.135
C_2	0.133	0.148	0.134	0.133	0.148	0.131
C_3	0.645	0.639	0.667	0.718	0.712	0.729
C_4	0.122	0.124	0.186	0.166	0.166	0.191
C_5	−0.451	−0.448	−0.377	−0.340	−0.340	−0.318
C_6	−0.410	−0.414	−0.430	−0.358	−0.361	−0.369
Energy/eV	−6.196	−6.203	−6.156	−6.306	−6.328	−6.183

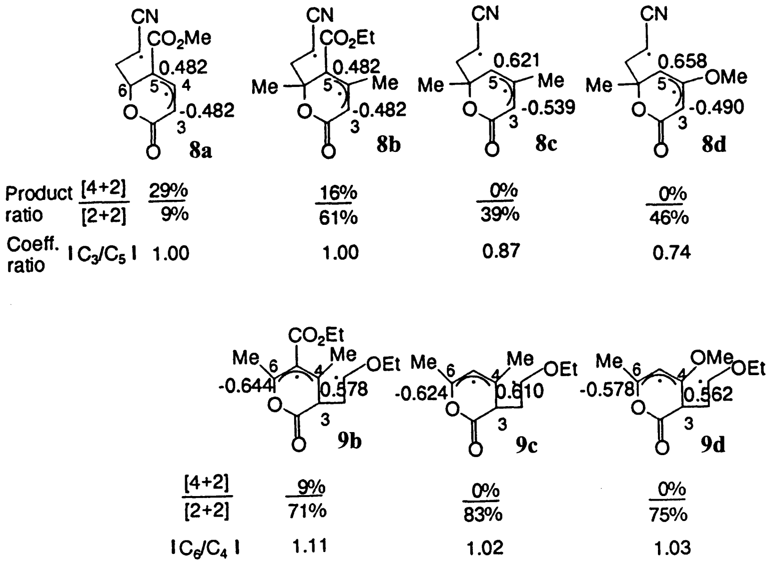


Fig. 2. Correlation between photoaddition periselectivity and SOMO coefficient ratios of radical intermediates by Hückel MO.

the photoadditions go through the respective intermediates in Scheme 1, and have the tendency of product change of Eq. 1 and the possibility of the adduct distribution in Table 1.

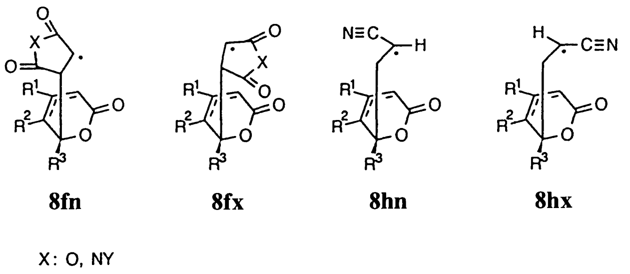
We estimated the excited triplet states of four 2-pyrones by means of AM1[10] and MNDO methods, also. The results of the frontier orbitals, the orbital functions and energies, are shown in Tables 4 and 5 together with the results of PM3. The three methods gave almost the same results in the points of the coefficient sizes and orders, and the energy values and the gaps except for a few data of MNDO.

We next discuss the [4+2] or [2+2]cycloaddition periselectivity of radicals **8** and **9**, namely formation of **3** or **4**, and **5** or **6** from each radical.

Figure 2 shows the results of product ratios [4+2]/[2+2], namely **3**/**4** or **6**/**5**, and coefficients of SOMO and the ratios C_3/C_5 or C_6/C_4 by the Hückel MO method. From the good correlation, the product ratios are inferred to be influenced by the coefficient ratios. Namely, relatively large coefficients of C_3 in SOMOs of the **8a** and **8b** radicals, and also of C_6 in SOMO of the **9b** radical are inferred to give periselectively [4+2]-cycloadducts **3** and **6**, too.

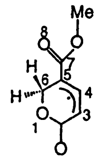
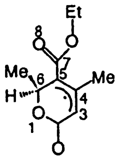
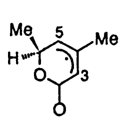
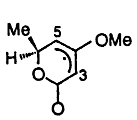
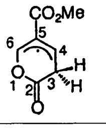
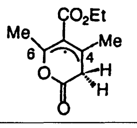
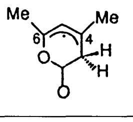
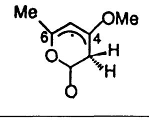
We also estimated optimized structures and molecular orbitals of radicals **8** and **9** by means of UHF-CI of PM3, AM1[10] and MNDO methods (Table 6). From the point of energies, the three methods gave similar data, but the sizes and orders of coefficients of the SOMOs were not in accord. Twist angles of C_4–C_5–C_7–O_8 of **8** by PM3 and MNDO methods were also large and were not consistent with the three methods. The large twist-angles mean twist between the pyrone ring and methoxycarbonyl group. They are not reasonable as the radical is at a ground state. The SOMO coefficient ratios, C_3/C_5 and C_6/C_4 also have a tendency to be opposite to those by the mentioned Hückel method and to photoadduct ratios. As the radicals are at ground states, the MO results are not reasonable. Some new considerations or alterations may be necessary for calculation of radicals by PM3 etc.

The next consideration is the stereochemistry of the photochemical [4+2]cycloadducts (**3**). **3bfx**, **3cfx**, **3agx**, **3bgx**, and **3cgx** were just *exo*-adducts, and photoadditions using **2h** gave both *exo*- and *endo*-adducts, **3ahx**, **3ahn**, **3bhx**, and **3bhn**. The HSOMO–LUMO or LSOMO–HOMO orbital interactions in Fig. 1 suggest step-wise and radical reactions via intermediates, **8fn**–**8hx** in Scheme 2 rather than concerted reactions. Existence of the twisted alkoxycarbonyl and methyl groups in excited **1** may cause steric hindrance for those *endo*-adducts to give *exo*-adducts. Preparation of both *endo*- and *exo*-adducts in the case of **2h** is inferred from the small steric hindrance between the alkoxycarbonyl and cyano groups. Orbital overlapping between HSOMO-C_4 on **1** and LUMO-$\underline{C}$(=N) on **2h** in Fig. 1 may also be favorable for the *endo*-adducts, **3ahn** and **3bhn**.



Scheme 2.

Table 6. MO Results of Radicals by PM3, AM1, and MNDO Methods

												
	PM3	AM1	MNDO	PM3	AM1	MNDO	PM3	AM1	MNDO	PM3	AM1	MNDO
SOMO C_5	0.667	0.653	0.678	0.644	0.624	0.636	0.661	0.661	0.662	0.655	0.660	0.666
C_3	−0.625	−0.600	−0.660	−0.619	−0.584	−0.615	−0.655	−0.658	−0.680	−0.653	−0.659	−0.678
Energy/eV	−5.955	−6.035	−5.911	−5.818	−5.953	−5.820	−5.412	−5.305	−5.372	−5.561	−5.485	−5.521
Twist Angle of 4–5–7–8/°	38.5	2.8	88.5	79.2	8.0	86.5						
												
	PM3	AM1	MNDO	PM3	AM1	MNDO	PM3	AM1	MNDO	PM3	AM1	MNDO
SOMO C_6	0.645	0.639	0.657	0.636	0.620	0.642	0.637	0.633	0.632	0.635	0.632	0.635
C_4	−0.668	−0.669	−0.658	−0.645	−0.649	−0.644	−0.646	−0.640	−0.654	−0.628	−0.619	−0.624
Energy/eV	−4.874	−4.802	−4.911	−4.673	−4.541	−4.886	−4.422	−4.328	−4.659	−4.206	−4.107	−4.339

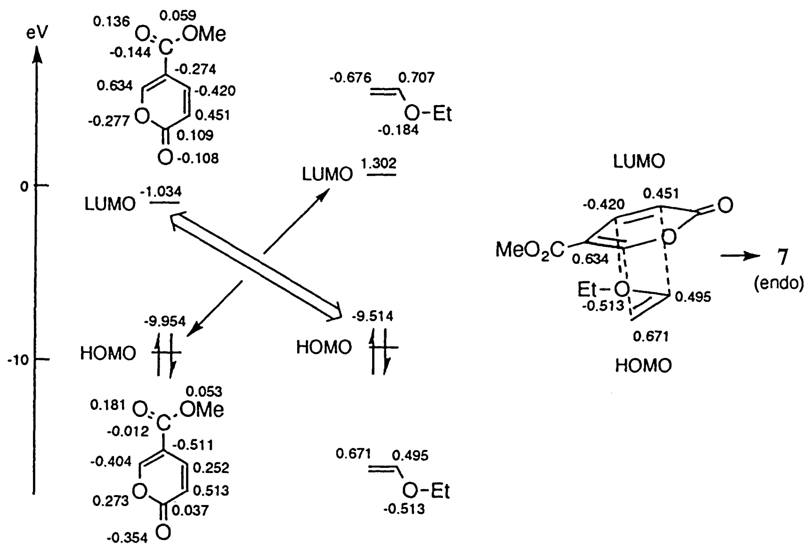


Fig. 3 Interpretation for preparation of the thermal regioselective *endo*-[4+2]cycloadduct **7** between ground states **1a** and **2i** by means of the PM3-CI method.

In conclusion, site- and regioselective [2+2]cycloadditions and regioselective [4+2]cycloadditions of triplet 2-pyrones were reasonably explained by use of the MO method.

We also show orbital consideration on the thermal [4+2]cycloaddition reaction of 2-pyrone **1a**.[11] Figure 3 interprets preparation of the thermal regio- and stereoselective adduct **7ai**. The energy gap (ΔE=8.48 eV) between LUMO of **1a** and HOMO of **2i** is smaller than the others. The frontier orbital interaction reveals that this thermal reaction is one of the reverse electron-demand Diels–Alder reactions and the addition-orientation and *endo*-selectivity comes from the very favorable orbital interactions of dotted lines.

Methods of Calculations

Calculations for Tables 2—6 and Figs. 1 and 3 were carried out on an IRIS4D/25GT computer at Chisso Petrochemical Co., and as software for the MNDO, AM1[10] and PM3[7] methods of QCPE program No. 455 (MOPAC Version 5.00) the interface of MOLGRAPH from Daikin Co. were driven. The software can give basic functions of energy minima of the respective molecules. The optimized structures of each triplet excited state of the 2-pyrones were calculated by using an unrestricted Hartree-Fock wave function (UHF), and the energies and coefficients were estimated by the CI method considering the thirty-six configurations. The optimized structures of the ground states of olefins and **1a** were calculated by a restricted one (RHF), and the energies and coefficients were estimated by CI calculations taking account of the 36 configurations.

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