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Remarkable interaction effects of molecular packing on site- and stereoselectivity in photocycloaddition of 2-pyrones with maleimide in the solid state

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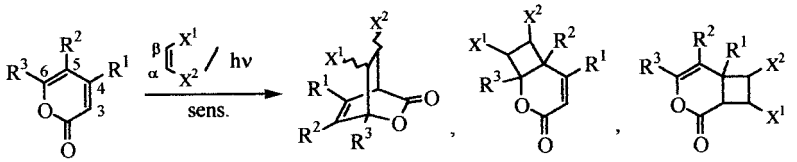
Abstract—Solid-state photoirradiation of 1:1 complex crystals of 4-[ω-(2-furyl)alkyloxy]-6-methyl-2-pyrones **1b**, **1c** or 4-(ω-arylalkyloxy)-6-methyl-2-pyrones **1d–j** with maleimide **2** gave [2+2]cycloadducts **3b–f**, **3i**, **3j** with exclusive stereoselectivity. The high reaction selectivity was confirmed by X-ray structure analyses and MO method of the complex crystals, which were composed of two sets of a 1:1 complex between **1** and **2**, arising from an CH–π interaction between **2** and the aromatic rings of **1**, and/or π–π stacking between the aromatic rings in addition to four kinds of hydrogen bonding between the ground state 2-pyrone moieties and **2**.

1. Introduction

Photochemical [2+2]cycloadditions in solution have been utilized to synthesize many kinds of important compounds.[1] The photoreactions were, however, not so regio- and stereoselective.[2] On the other hand, organic solid-state photoreactions are strictly controlled by their crystal structures and can therefore be highly selective. Single- and two-component organic crystals recently supplied ideal surroundings for controlling the selectivity of photochemical reactions because of the tight and regular arrangement of the molecules in the crystals,[3] using a noncovalent interaction like a hydrogen bond, charge transfer interaction, or π–π stacking. Much attention has been paid to the [2+2]- and [4+4] photodimerization reactions[3] in the crystals including the asymmetric synthesis in host–guest inclusion complexes[4] together with intramolecular cyclization[5] and valence isomerization,[6] but only limited



R^1	R^2	R^3	X^1	X^2
H	CO_2Me	H	COOCO	
Me	CO_2Et	Me	CO(NH)CO	
Me	H	Me	H	CN
OMe	H	Me	H	OEt

Scheme 1.

Keywords: solid-state photochemistry; cycloaddition; 2-pyrones; hydrogen bonding; CH–π interaction; π–π stacking.

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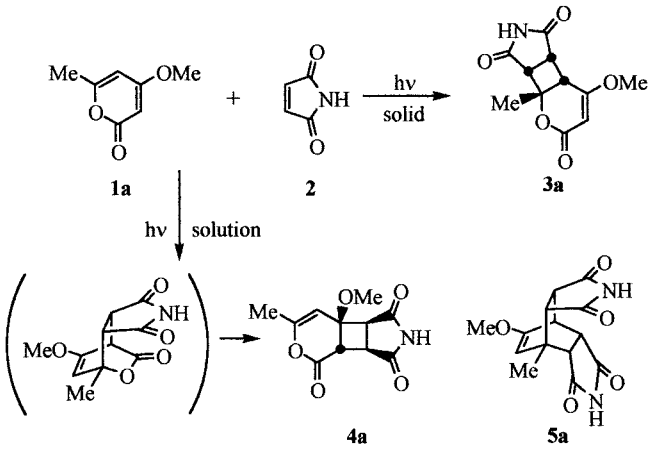
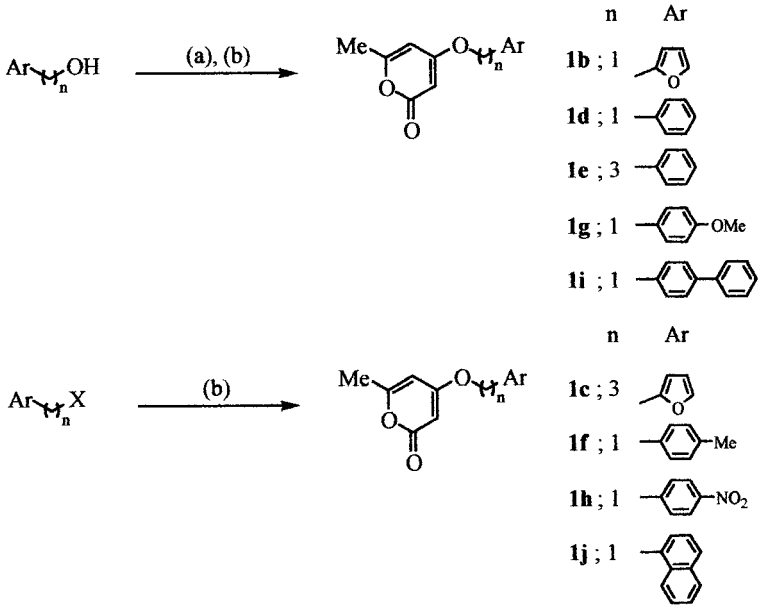


Scheme 2.



Scheme 3. Conditions: (a) PPh_3, CCl_4; (b) 4-hydroxy-6-methyl-2-pyrone, DBU.

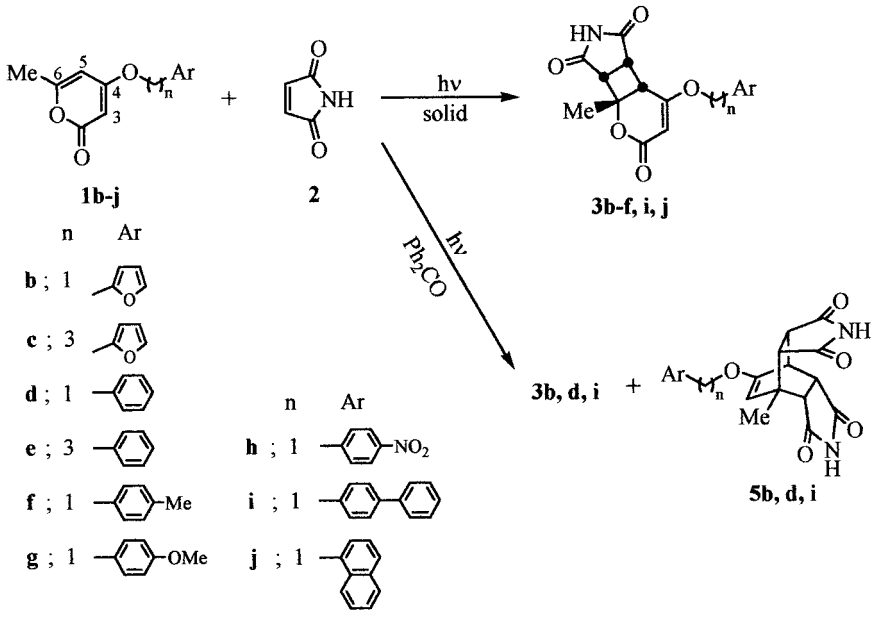
investigation of [2+2] cycloaddition between two different organic molecules has been reported.[7]

We have reported, as shown in Scheme 1,[8] that the peri-([2+2] or [4+2]), site-(3,4- or 5,6-addition) and regio-selective photoadducts in the triplet photoreactions of 2-pyrones with electron-deficient or electron-rich alkenes in solution were considered to be formed through the regio-selective 3-β or 6-β two-center interaction at the first-step, and periselective ring-closure from the biradical intermediates. The two-step cycloaddition selectivities were, however, not so high. We showed recently that the solid-state photocycloaddition reaction of 4-methoxy-6-methyl-2-pyrone **1a** with maleimide, gave a [2+2]cycloadduct, peri-, site-, and stereo-selectively, by using hydrogen bonding between **1a** and **2** (Scheme 2).[9] Overlapping or short distance between the two substrates and also some substituents of the substrates in the solid state may control the cross-photocycloaddition. We planned photoreactions between 4-[ω-(2-furyl)alkyloxy]-6-methyl-2-pyrones (**1b**, **1c**) or 4-(ω-arylalkyloxy)-6-methyl-2-pyrones (**1d–j**) and maleimides, using their intermolecular multiple interactions to control the molecular packing. Correlation between the mutual geometry of some groups in the complex crystals and the photochemical behavior may be analyzed by X-ray crystal analyses.

Table 1. Melting points of the starting materials and 1:1 complex crystals prepared by the method

2 Pyrone (°C)	1:1 Complex crystal (°C)
1d (83–85)	**1d·2** (99–101)
1f (68–72)	**1f·2** (75–77)
1i (142–143)	**1i·2** (140–141)
1j (119–120)	**1j·2** (109–110)

Maleimide (mp 92–94°C).



Scheme 4.

2. Results and discussion

2.1. Synthesis of compounds 1b–j

2-Pyrones, **1b–j**, were prepared by dehydrohalogenative coupling between 4-hydroxy-6-methyl-2-pyrone and halogenated alkylaromatic compounds with a base in 27–71% yields (Scheme 3).

2.2. Preparation of 1:1 complex crystals

1:1 Complex crystals of 2-pyrones **1** with maleimide **2** were prepared by three methods of the two equimolar substrates: (a) crystallization from an appropriate solvent; (b) evaporation of the solvent from a solution containing the substrates; (c) grinding the substrates with a mortar and pestle.[10] The melting points of the crystals obtained by method (a) showed higher values than that of both or one substrate (Table 1).

2.3. Photochemical results

Irradiation of a 1:1 complex crystal **1d·2** (1.0 mmol) (colorless prisms, mp 99–101°C) between **1d** (mp 83–85°C) and **2** (mp 92–94°C), which was prepared by the crystallization method (a) from a $CHCl_3$ solution, at room temperature for 24 h gave [2+2]cycloadduct **3d** in 70% yield as the sole product together with recovery of **1d·2** (23%) (Scheme 4). The structure of **3d** was established fully by spectroscopic data (IR, MS and ^1H and ^{13}C NMR; see Section 4) and determined by an X-ray structure analysis. Similar irradiation of the 1:1 complex crystals **1f·2**, **1i·2**, and **1j·2** afforded [2+2]cycloadducts **3f**, **3i** and **3j** in 90, 52 and 65% yields, respectively, with each recovery of **1·2**. The structure of **3f** was also determined by single-crystal X-ray diffraction. It was difficult to prepare the 1:1 complex crystals of **1b·2**, **1c·2**, **1e·2**, **1g·2** and **1h·2** by the crystallization method (a). Irradiation of the mixtures of **1b** and **2**, **1c** and **2**, **1e** and **2**, **1g** and **2**, and **1h** and **2** prepared by method (b) gave [2+2]cycloadducts **3b**, **3c** and **3e** in 100, 45 and 82% yields, respectively, with recovery of **1c·2** and **1e·2**. Neither method (b) nor (c) afforded photocycloadduct of **1g** with **2** or **1h**

Table 2. Grinding-time effect for photocycloadditions of the mixtures between 2-pyrones and maleimide

Grinding time (min)	Yield of **3** (%)[a]				
	3d	**3e**	**3f**	**3i**	**3j**
5	81	66	81	59	39
10	89	72	90	63	43
30	96	74	90	89	89

All mixtures of **1d**, **1e**, **1f**, **1i** and **1j** (0.50 mmol) with **2** (0.50 mmol) were ground for 5–30 min and irradiated for 24 h.
[a] Yields were calculated by ^1H NMR and no other product formed.

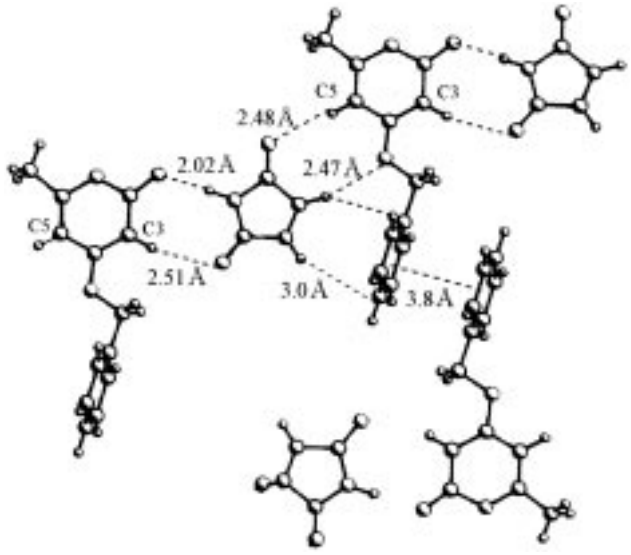


Figure 1. Molecular packing diagram by hydrogen bondings, CH–π, and π–π interactions in the 1:1 complex crystal of **1d** with **2**.

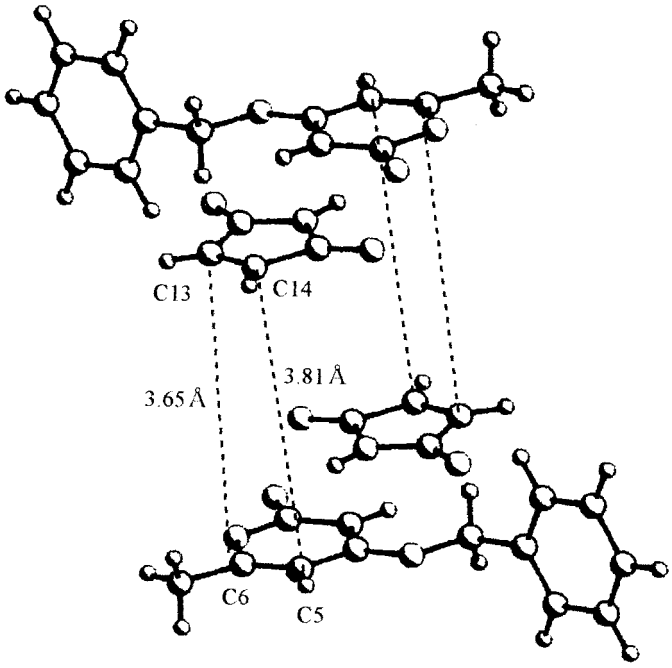


Figure 2. Molecular packing diagram of the 1:1 complex crystal of **1d** with **2**.

with **2**. The yields of the products **3d**, **3e**, **3f**, **3i** and **3j** were increased by longer irradiation and prolonged mixing time of the mixtures using method (c) (Table 2). This means intermolecular interactions in this system are very effective for the molecular packing.

2.4. X-Ray analyses of the complex crystals and the photochemical behavior

The reaction selectivity in the solid-state photoreactions of 1:1 complex crystals **1d·2**, **1f·2**, **1i·2** and **1j·2** can be viewed from X-ray crystallographic analyses of the single crystals, which were prepared by crystallization from $CHCl_3$, CH_2Cl_2 or MeCN, as a consequence of the crystal topology. In the case of **1d·2**, as can be seen in Fig. 1, the crystals contain hydrogen bondings between the O–C═O and HN groups with the O···H distance of 2.02 Å, together with C(4)═C(3)H···O═C–N (2.51 Å), C(6)═C(5)H···O═C–N (2.48 Å) and 2-pyrone–O(ether)···HC═(maleimide) (2.47 Å) (the last two hydrogen bondings were recognized newly). The CH···O type of hydrogen bonding in the crystal has been recognized as an important interaction in determining the molecular packing.[11] CH–π interactions, which have been suggested to play important roles in the crystal structure of host–guest compounds,[12] between the maleimide olefin and benzene (3.0 Å), and π–π stacking between two benzene rings (3.8 Å) were also observed. These hydrogen bondings were suggested from the lower wavelength shifts of the carbonyl groups in the IR spectra: lactone and imide carbonyls showed 17 and 13 cm^{-1} shifts, respectively, from each original absorption band. It is considered that these weak interactions afforded the higher melting points of the 1:1 complex crystals than that of each substrate. The angles between reactive olefin carbons in **1d** and **2** are 102.7° (C(6)–C(5)–C(14)), 75.0° (C(5)–C(6)–C(13)), 111.5° (C(6)–C(13)–C(14)), 68.8° (C(5)–C(14)–C(13)), and intermolecular distances of the two reacting double bonds are 3.65 Å (C(6)···C(13)) and 3.81 Å (C(5)···C(14)), which are within the normal photoreaction distances in the solid state[13] (Fig. 2). Such crystal structure is inferred to be effectively brought about by four types of hydrogen bondings, two-layer electrostatic interactions between the 2-pyrone ring and **2**, and π–π stacking between two benzene rings, which is in contrast to the fact that pure benzene adopts a CH–π interaction structure[14] and the structure of the benzene–hexafluorobenzene material is composed of π–π stacking of alternating molecules in the solid state.[15,16] The π–π stacking arrangement of tethered benzene rings in this study is inferred to be caused by the packing effect around the benzene rings. On the other hand, a CH–π interaction was observed between **2** and the benzene ring of **1** (Fig. 1). Although the CT complex absorption band of **1d·2** was not observed from the UV measurements in the solid phase and in solution, the overlapping structure of **1d** with **2** in the crystal is inferred to be formed by the electrostatic interaction. The solid-state photoreaction of the complex crystal **1a** with **2** gave a [2+2]cycloadduct,[9] but that of 4,6-dimethyl-2-pyrone with **2** did not afford the cycloadduct. 2-Pyrone–O(ether)···HC═(maleimide) (2.47 Å) hydrogen bonding is considered to be necessary for the photocycloaddition. It may work to orient the two reactive double bonds sterically.

X-ray crystallographic analyses of **1i·2** and **1j·2** showed results similar to those of **1d·2** with respect to bond distances between the reacting double bonds, hydrogen bonds, CH–π interaction between **2** and the benzene ring, and π–π stacking between the aromatic rings (Figs. 3 and 4). These results are summarized in Table 3. On the other hand, as can be seen in Fig. 5, X-ray crystallographic analysis of **1f·2** showed a CH–π interaction between the benzene rings instead of the π–π stacking shown in **1d·2**, **1i·2** and **1j·2**. The fact that the calculated density value of the 1:1 complex crystal **1f·2** (1.280 g cm^{-3}) became smaller than

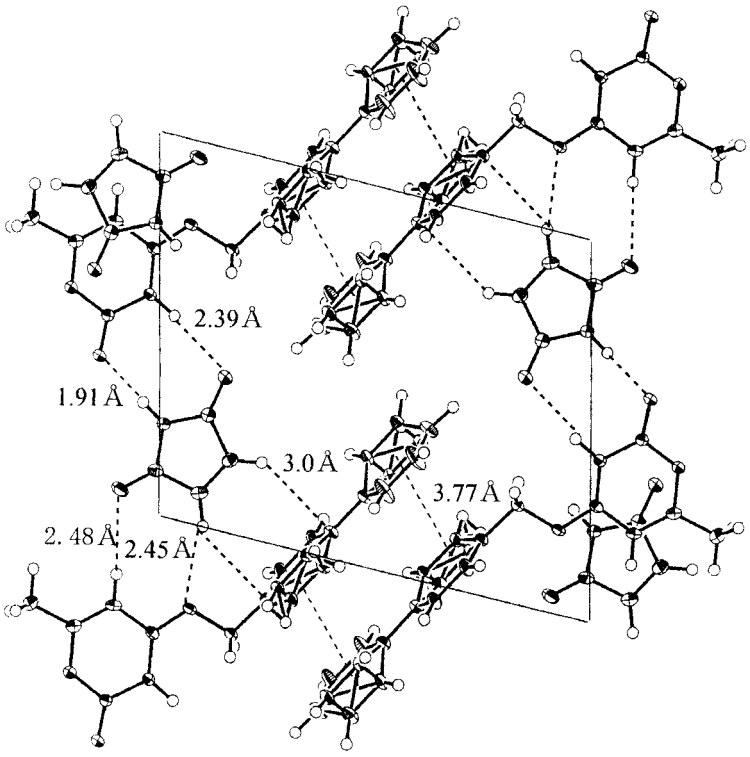


Figure 3. Molecular packing diagram by hydrogen bondings, CH–π, and π–π interactions in the 1:1 complex crystal of **1i** with **2**.

that of **1d·2** (1.330 g cm^{-3}) from the X-ray crystal data. A comparison of the packing diagram of the **1f·2** with the other complex crystals suggested an enlargement of the vacant space between **1f** and **2** owing to the steric hindrance of a *p*-methyl group at the benzene ring. The *p*-phenyl group of **1i·2** (1.387 g cm^{-3}) stacked with another molecule of **1i** prefer steric hindrance to give a tight packing structure (Fig. 3). Preparation of the 1:1 complex crystal of **1g**

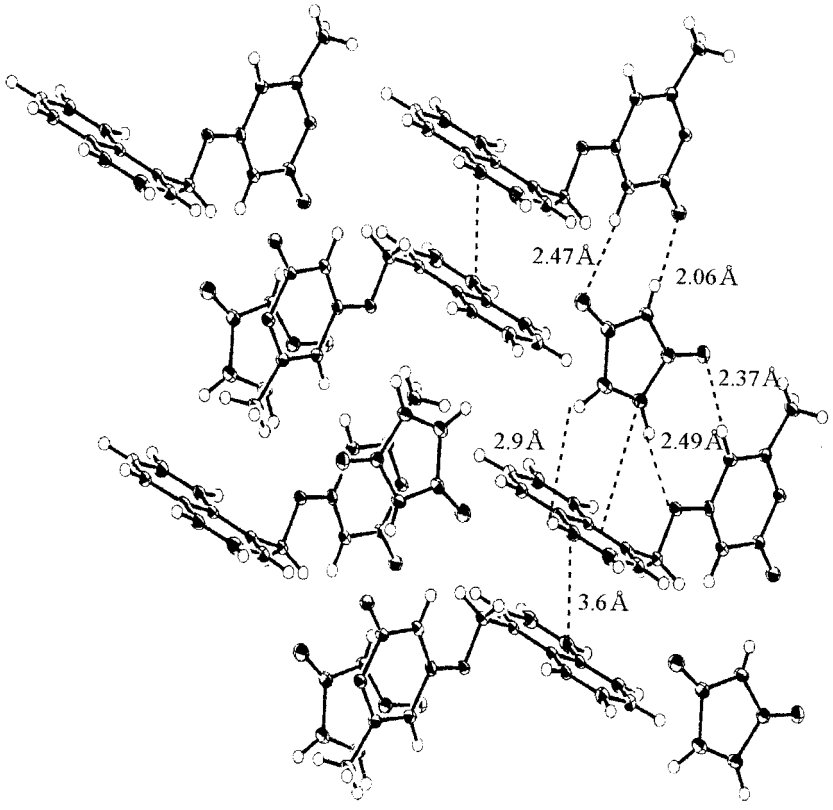


Figure 4. Molecular packing diagram by hydrogen bondings, CH–π, and π–π interactions in the 1:1 complex crystal of **1j** with **2**.

Table 3. Features of 1:1 complex crystals **1d·2**, **1f·2**, **1i·2** and **1j·2** from the X-ray structure analyses

	Distances between two reacting double bonds (Å)	Hydrogen bonds (Å)	Interaction of aromatic–aromatic rings (distance, Å)	Interaction of aromatic ring–maleimide (distance, Å)
1d·2	3.65, 3.81	2.02[a] 2.51[b] 2.48[c] 2.47[d]	π–π (3.8)	CH–π (3.0)
1f·2	3.65, 3.77	2.02[a] 2.42[b] 2.51[c] 2.55[d]	CH–π	CH–π (3.0)
1i·2	3.52, 3.70	1.91[a] 2.39[b] 2.48[c] 2.45[d]	π–π (3.8)	CH–π (3.0)
1j·2	3.49, 3.57	2.06[a] 2.47[b] 2.37[c] 2.49[d]	π–π (3.6)	CH–π (2.9)

[a] C(2)═O···HN.
[b] C(3)–H···C═O.
[c] ═C(5)–H···O═C(maleimide).
[d] Pyrone–O···HC═(maleimide).

(*p*-methoxyphenyl group) or **1h** (*p*-nitrophenyl group) with **2** was difficult despite many crystallization trials and the mixtures of **1g** and **2**, and **1h** and **2** were also found to be completely photostable, even after photolysis for 48 h. Since the crystal packing depends on numerous polar interactions, the change in the crystal structure owing to the polar nature of the methoxy or nitro group seems to prevent the favorable parallel orientation of the two sets of 1:1 complex between **1** and **2** such that a photocycloaddition reaction is precluded.

The photoreactions of **1b–j** with *N*-methylmaleimide and *N*-phenylmaleimide, whose substrates gave no 1:1 complex crystals with **1b–j**, did not afford cycloadduct in the solid state. The substrates were also almost inactive with **1b–j** in solution photoreaction. On the other hand, sensitized photoirradiation to a solution of **1i** and maleimide **2**, whose solid-state photoreaction afforded only **3i**, gave *exo–endo* bis-adduct **5i** in 13% yield, which was formed through decarboxylation of the [4+2]cycloadduct followed by addition of another molecule of **2**,[9] in addition to **3i** (9%) and unidentified compounds. Similar sensitized photoreactions of **1b**, **1d** with **2** gave bis-adducts **5b**, **5d** as major products. These results suggest that the arrangement in parallel orientation by the C═O···HN hydrogen bonding control the photocycloaddition reaction in the solid state.

The arrangement of **1** and **2** in the crystal is explained by some electrostatic interactions including hydrogen bonding of the two substrates at the ground state. The interactions are confirmed by the calculated atomic charges of the ground states of **1d** and **2** as shown in Fig. 6. It shows four kinds of hydrogen bonding interactions, a CH–π interaction between **2** and the benzene ring, and overlapping between electronegative C(5) of **1d** and an electropositive carbonyl carbon of **2**. The overlapping distance is observed to be

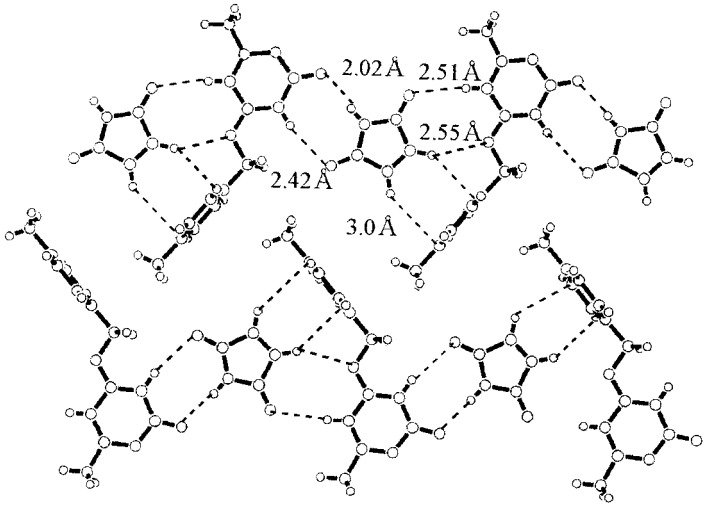


Figure 5. Molecular packing diagram by hydrogen bondings, CH–π interactions in the 1:1 complex crystal of **1f** with **2**.

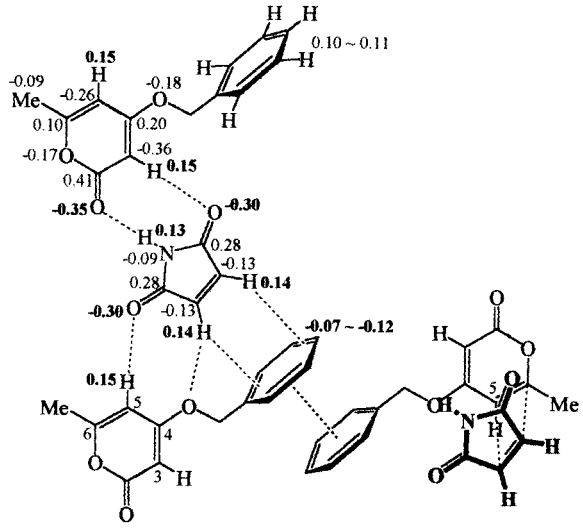


Figure 6. Calculated atomic charges of the two ground states of **1d** and **2**, and their interactions.

3.89 Å from the X-ray crystallographic analysis. On the basis of these results, photocycloaddition reactions of **1** with **2** in the solid state shown in Scheme 4 are confirmed to be exclusively peri-, site- and stereo-selective.

3. Conclusions

This work revealed interesting multiple factors of 1:1 complex crystals **1·2**, which served as photoreactive molecules in the solid state. The combination of four kinds of hydrogen bondings, CH–π interaction, π–π stacking and electrostatic interaction in the ground state arranged the two sets of molecules between two layers and oriented the reactive C5–C6 double bond of the 2-pyrone ring with the olefinic moiety of maleimide. Thus, highly stereoselective photocycloaddition reactions were possible (the two olefins were nearly parallel and separated by less than 4.0 Å). Of the nine crystalline materials prepared by three methods (crystallization, evaporation of the solvent, and grinding of the two substrates), all but two (**1g** and **1h** with **2**) underwent the anticipated photocycloaddition reactions. The stereochemistry of the photocycloadduct and/or X-ray structural analysis of the 1:1 complex crystals **1·2** revealed the stacked interaction between **1** and **2** in the crystals. This favorable molecular feature should prove promising in the application of this concept to other olefin systems for stereochemically controlled [2+2]photocycloadditions in the solid state.

4. Experimental

4.1. General

All melting points are uncorrected. NMR spectra were measured at 400 MHz on the JNM GSX-400 (TMS as an internal standard). IR spectra were recorded with a JASCO IR Report-100 spectrometer as KBr disks. Mass spectra were recorded with a JEOL LMS-OISG or a JEOL JMS-HX110A (FAB MS) using *m*-nitrobenzyl alcohol as matrix. Elemental analyses were made using a Yanaco MT-5. Photoirradiations were carried out in a Pyrex tube by using Riko 400 W high pressure mercury lamp equipped with a merry-go-round apparatus.

4-[3-(2-Furylpropoxy)]-6-methyl-2-pyrone (**1c**) was prepared according to the method described in the literature.[17] Single crystal X-ray diffraction analysis of **1d·2** was performed on an Enraf–Nonius CAD4 diffractometer, and those of **1f·2**, **1i·2**, **1j·2**, **3d**, **3e**, **3f** were performed on a Rigaku RAXIS-RAPID Imaging diffractometer with graphite-monocromated Mo Kα radiation. Lorentz and polarization corrections were applied to the intensity data. The structures were solved by direct methods using SIR92[18] or SIR88[19] and refined by a full-matrix least-squares method. The non-hydrogen atoms were refined isotropically. All calculations were performed using the TEXSAN[20] crystallographic software package.†

4.1.1. 4-(2-Furyloxy)-6-methyl-2-pyrone (1b). A solution of furfuryl alcohol (6.6 g, 67 mmol) and triphenylphosphine (21 g, 80 mmol) in CCl_4 (60 ml) was refluxed for 70 min under nitrogen atmosphere. The solution was allowed to cool to room temperature, and hexane (100 ml) was added. Resulting solid was filtered and the filtrate was evaporated. A solution of the concentrate in MeCN (50 ml) was added to 4-hydroxy-6-methyl-2-pyrone (6.3 g, 50 mmol), then DBU (9.7 g, 64 mmol) was added dropwise and refluxed for 19.5 h. The solution was evaporated and submitted to column chromatography (silica gel, ethyl acetate–hexane=1:1) to give **1b**, which was purified by recrystallization from hexane. **1b** (2.7 g, 27% yield): mp 110–111.5°C; IR (KBr) 1734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20 (3H, s), 4.96 (2H, s), 5.55 (1H, s), 5.79 (1H, s), 6.41 (1H, m), 6.48 (1H, m), 7.47 (1H, m); LR MS *m/z* 206 (M^+). Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 63.97; H, 4.87.

4.1.2. 4-Benzyloxy-6-methyl-2-pyrone (1d). 1d was prepared according to a similar method mentioned above by using benzyl alcohol (7.2 g, 67 mmol), triphenylphosphine (21 g, 81 mmol), CCl_4 (60 ml), 4-hydroxy-6-methyl-2-pyrone (6.3 g, 50 mmol) and DBU (9.7 g, 64 mmol). **1d** (3.8 g, 35% yield): mp 83–84°C; IR (KBr) 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.21 (3H, s), 5.01 (2H, s), 5.50 (1H, s), 5.84 (1H, s), 7.3–7.5 (5H, m); LR MS *m/z* 216 (M^+). Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.27; H, 5.60.

4.1.3. 4-(3-Phenylpropoxy)-6-methyl-2-pyrone (1e). 1e was prepared by a method similar to that of **1b** by using 3-phenyl-1-propanol (9.1 g, 67 mmol), triphenylphosphine (21 g, 81 mmol), CCl_4 (60 ml), 4-hydroxy-6-methyl-2-pyrone (6.3 g, 50 mmol) and DBU (9.7 g, 64 mmol). **1e** (4.0 g, 32% yield): mp 79–80°C; IR (KBr) 1708 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.08 (2H, quint, J=6.8 Hz), 2.21 (3H, s),

† Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK and copies can be obtained on request, free of charge, by quoting the publication citation and deposition numbers 151239-151245 for **1d·2**, **1f·2**, **1i·2**, **1j·2**, **3d**, **3e** and **3f**, respectively.

2.76 (2H, t, J=6.8 Hz), 3.92 (2H, t, J=6.8 Hz), 5.34 (1H, s), 5.79 (1H, s), 7.16–7.32 (5H, m); LR MS m/z 244 (M^+). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.68; H, 6.60.

4.1.4. 4-(4-Methylbenzyloxy)-6-methyl-2-pyrone (1f). A solution of *p*-methylbenzyl chloride (7.0 g, 50 mmol), 4-hydroxy-6-methyl-2-pyrone (6.3 g, 50 mmol) and DBU (9.7 g, 64 mmol) in MeCN (50 ml) was refluxed for 19.5 h. The solution was allowed to cool to room temperature, and was evaporated. The concentrate was submitted to column chromatography (silica gel, ethyl acetate–hexane= 1:1) to give **1f**, which was purified by recrystallization from hexane–ethanol (1:1). **1f** (4.6 g, 40% yield): mp 68–72°C; IR (KBr) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20 (3H, s), 2.37 (3H, s), 4.97 (2H, s), 5.52 (1H, s), 5.82 (1H, s), 7.20 (2H, d, J=7.6 Hz), 7.26 (2H, d, J=7.6 Hz); LR MS m/z 230 (M^+). Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.13; H, 6.12.

4.1.5. 4-(4-Methoxybenzyloxy)-6-methyl-2-pyrone (1g). **1g** was prepared by a method similar to that of **1b** by using 4-methoxybenzyl alcohol (9.2 g, 67 mmol), triphenylphosphine (21 g, 80 mmol), CCl_4 (60 ml), 4-hydroxy-6-methyl-2-pyrone (6.3 g, 50 mmol) and DBU (9.7 g, 64 mmol). **1g** (4.0 g, 32% yield): mp 109–112°C; IR (KBr) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20 (3H, s), 3.83 (3H, s), 4.93 (2H, s), 5.50 (1H, s), 5.80 (1H, s), 6.92 (2H, d, J=8.4 Hz), 7.30 (2H, d, J=8.4 Hz); LR MS m/z 246 (M^+). Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.29; H, 5.76.

4.1.6. 4-(4-Nitrobenzyloxy)-6-methyl-2-pyrone (1h). 1h was prepared by a method similar to that of **1f** by using *p*-nitrobenzyl bromide (6.48 g, 30 mmol), 4-hydroxy-6-methyl-2-pyrone (3.78 g, 30 mmol) and DBU (5.6 g, 36 mmol). **1h** (2.7 g, 34% yield): mp 164–167°C; IR (KBr) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.24 (3H, s), 5.12 (2H, s), 5.46 (1H, s), 5.88 (1H, s), 7.55 (2H, J=8.0 Hz), 8.28 (2H, d, J=8.0 Hz); LR MS m/z 262 (M+1). HR FAB MS (M+1) Calcd for $C_{13}H_{12}NO_5$ 262.0175. Found 262.0174.

4.1.7. 4-(4-Biphenyloxy)-6-methyl-2-pyrone (1i). 1i was prepared by a method similar to that of **1b** by using 4-biphenylmethanol (5.5 g, 30 mmol), triphenylphosphine (9.5 g, 36 mmol), CCl_4 (50 ml), 4-hydroxy-6-methyl-2-pyrone (3.8 g, 30 mmol) and DBU (5.6 g, 36 mmol). **1i** (2.4 g, 27% yield): mp 142–143°C; IR (KBr) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.22 (3H, s), 5.04 (2H, s), 5.52 (1H, s), 5.85 (1H, s), 7.3–7.6 (9H, m); LR MS m/z 292 (M^+). Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.04; H, 5.54.

4.1.8. 4-(1-Naphthylmethyloxy)-6-methyl-2-pyrone (1j). **1j** was prepared by a method similar to that of **1f** by using (1-chloromethyl)naphthalene (8.8 g, 50 mmol), 4-hydroxy-6-methyl-2-pyrone (6.3 g, 50 mmol) and DBU (9.7 g, 64 mmol). **1j** (4.1 g, 30% yield): mp 119–120°C; IR (KBr) 1708 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20 (3H, s), 5.44 (2H, s), 5.67 (1H, s), 5.82 (1H, s), 7.4–7.9 (7H, m); LR MS m/z 266 (M^+). Anal Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.69; H, 5.30.

4.2. Typical procedures of 1:1 complex crystal preparation.

(a) 2-pyrone **1** (0.50 mmol) and maleimide **2** (0.50 mmol) were dissolved in hot $CHCl_3$, CH_2Cl_2 or MeCN. The solution was allowed to cool slowly to room temperature, during which fine crystals were formed. (b) Acetone solution of **1** (0.50 mmol) and **2** (0.50 mmol) in a Pyrex tube was evaporated using rotary evaporator at room temperature. (c) A mixture of **1** (0.50 mmol) and **2** (0.50 mmol) was ground together in a mortar and for 30 min.

4.3. 1b·2 1:1 Complex crystal

Since the preparation of 1:1 complex crystal by method (a) is difficult, treatment of a solution of **1b** (41 mg, 0.20 mmol) and **2** (20 mg, 0.20 mmol) in acetone (5 ml) by method (b) gave **1b·2**. Mp 101–104°C.

4.3.1. 11-(2-Furfuryloxy)-7-methyl-8-oxa-4-azatricyclo-[5.4.0.0^{2,6}]undec-10-en-3,5,9-trione (3b) from the photolysis of 1b·2. Crystals of **1b·2** (60 mg, 0.20 mmol) were photolyzed in a Pyrex tube for 24 h under nitrogen atmosphere at room temperature. ^1H NMR revealed quantitative conversion to cycloadduct **3b**, which was recrystallized from MeCN. Mp 170–173°C; IR (KBr) 3450, 1780,1735, 1710 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.58 (3H, s), 3.41 (1H, d, J=6.0 Hz), 3.51 (1H, dd, J=6.0, 9.2 Hz), 3.64 (1H, d, J=9.2 Hz), 4.82 (1H, d, J=12.4 Hz), 5.02 (1H, d, J=12.4 Hz), 5.46 (1H, s), 6.50 (1H, m), 6.60 (1H, m), 7.73 (1H, m); LR MS m/z 303 (M^+). Anal. Calcd for $C_{15}H_{13}NO_6$: C, 59.41; H, 4.32, N, 4.62. Found: C, 59.65; H, 4.37; N, 4.55.

4.4. 1c·2 1:1 Complex crystal

Treatment of a solution of **1c** (1.0 mmol) and **2** (1.0 mmol) in acetone (5 ml) by method (b) gave **1c·2** as a colorless oil, which was solidified at −15°C.

4.4.1. 11-(2-Furfurylpropoxy)-7-methyl-8-oxa-4-azatricyclo[5.4.0.0^{2,6}]undec-10-en-3,5,9-trione (3c) from the photolysis of 1c·2. Crystals of **1c·2** (330 mg, 1.0 mmol) were photolyzed in a Pyrex tube at −15°C for 24 h. The reaction solid was washed with $CHCl_3$ (5 ml) to remove the starting materials and the resulting solid was filtered to give **3c** (149 mg, 45% yield), which was recrystallized from MeCN. The starting material **1c·2** was recovered from the concentration of the $CHCl_3$ filtrate (47%). Mp 226–228°C; IR (KBr) 3400, 1780, 1730, 1700 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.59 (3H, s), 1.93 (2H, quint, J=7.8 Hz), 2.72 (2H, t, J=7.8 Hz), 3.41 (1H, d, J=6.2 Hz), 3.53 (1H, dd, J=6.2, 9.2 Hz), 3.63 (1H, d, J=9.2 Hz), 3.83 (1H, dt, J=7.8, 10.2 Hz), 3.95 (1H, dt, J=7.8, 10.2 Hz), 5.24 (1H, s), 6.15 (1H, m), 6.35 (1H, m), 7.52 (1H, m), 11.44 (1H, s); LR MS m/z 332 (M+1). Anal. Calcd for $C_{17}H_{17}NO_6$: C, 61.63; H, 5.17; N, 4.23. Found: C, 61.47; H, 5.21; N, 4.30.

4.5. 1d·2 1:1 Complex crystal

A mixture of **1d** (109 mg, 0.50 mmol) and **2** (49 mg, 0.50 mmol) was dissolved in 5 ml of hot $CHCl_3$. The solution was allowed to cool at room temperature, during which

fine white crystals were formed. After crystallizing overnight, the crystal were collected by filtration, then dried in vacuo to give **1d·2** (148 mg, 94% yield, mp 99–101°C) as colorless prisms. ^{1}H NMR confirmed a 1:1 ratio of **1d·2**.

4.6. Single crystal X-ray diffraction analysis of 1d·2

Crystal structure data for **1d·2**: formula $C_{17}H_{15}NO_5$. M=313.31, crystal dimensions 0.07×0.20×0.55 mm, triclinic, space group P-1 (#2), a=6.5888 Å, b=11.2920 Å, c=11.8837 Å, α=64.8883°, β=78.1222°, γ=82.2622°, V=782.3323 Å^3, Z=2, ρ_{calcd}=1.330 g cm^{-3}, $2\theta_{max}$=49.2°, T=296.0 K, R (R_w)=0.063 (0.099) for 1119 reflection data with $I>3.00\sigma(I)$ and 269 variables, GOF=1.36.

4.6.1. 11-Benzyloxy-7-methyl-8-oxa-4-azatricyclo[5.4.0.0^{2,6}]-undec-10-en-3,5,9-trione (3d) from the photolysis of 1d·2. Crystals of **1d·2** (148 mg, 0.48 mmol) prepared by method (a) were sandwiched with two Pyrex glass plates and photolyzed for 24 h under nitrogen atmosphere at room temperature. The same workup, as mentioned above, afforded **3d** (105 mg, 70% yield) together with recovery of **1d·2** (23%). Similar irradiations to the crystals **1d·2** (0.50 mmol) prepared by method (c), grinded for 30 min gave **3d** in 96% yield. Mp 266–268°C; IR (KBr) 3300, 1775, 1720, 1690 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 1.60 (3H, s), 3.42 (1H, d, J=6.4 Hz), 3.54 (1H, dd, J=6.4, 9.8 Hz), 3.69 (1H, d, J=9.8 Hz), 4.84 (1H, d, J=7.8 Hz), 5.00 (1H, d, J=7.8 Hz), 5.40 (1H, s), 7.3–7.5 (5H, m), 11.48 (1H, s); ^{13}C NMR (DMSO-d$_6$) d 26.1, 39.2, 39.4, 51.1, 69.4, 75.4, 89.9, 126.8, 126.9, 133.5, 161.7, 166.6, 173.3, 175.3; LR MS m/z 314 (M+1); HR FAB MS (M+1) Calcd for $C_{17}H_{15}NO_5$ 314.1029. Found 314.1029.

4.6.2. Single crystal X-ray diffraction analysis of 3d. Crystal structure data for **3d**: formula $C_{17}H_{15}NO_5$. M=313.31, crystal dimensions 0.07×0.20×0.10 mm, triclinic, space group P-1 (#2), a=10.769(2) Å, b=11.796(2) Å, c=6.381(1) Å, α=101.192(4)°, β=105.520(6)°, γ=68.591(7)°, V=723.0(2) Å^3, Z=2, ρ_{calcd}=1.439 g cm^{-3}, $2\theta_{max}$=55.0°, T=93.0 K, R (R_w)=0.055 (0.091) for 1929 reflection data with $I>3.00\sigma(I)$ and 269 variables, GOF=1.31.

4.7. 1e·2 1:1 Complex crystal

Treatment of a solution of **1e** (1.0 mmol) and **2** (1.0 mmol) in acetone (5 ml) by method (b) gave **1e·2** (mp 74–76°C).

4.7.1. 11-(3-Phenylpropyloxy)-7-methyl-8-oxa-4-azatricyclo[5.4.0.0^{2,6}]undec-10-en-3,5,9-trione (3e) from the photolysis of 1e·2. Crystals of **1e·2** (343 mg, 1.0 mmol) prepared by method (b) were photolyzed in a Pyrex tube for 24 h at room temperature. The same workup afforded **3e** (279 mg, 82% yield) and recovery of **1e·2** (10%). Similar irradiation to the crystals **1e·2** (0.50 mmol) prepared by method (c), grinded for 30 min gave **3e** (74% yield), which was recrystallized from DMF, together with recovery of **1e·2** (18%). Mp 235–237°C; IR (KBr) 3250, 1770, 1720, 1695 cm^{-1}, ^{1}H NMR (DMSO-d$_6$) δ 1.59 (3H, s), 1.91 (2H, quint, J=6.4 Hz), 3.41 (1H, d, J=6.2 Hz), 3.53 (1H, dd, J=6.2, 9.2 Hz), 3.63 (1H, d, J=9.2 Hz), 3.81 (1H, dt, J=6.4, 10.0 Hz), 3.93 (1H, dt, J=6.4, 10.0 Hz), 4.01 (2H, t, J=6.4 Hz), 5.23 (1H, s), 7.2–7.3 (5H, m), 11.45 (1H, s); ^{13}C NMR (DMSO-d$_6$) δ 26.1, 28.2, 29.7, 39.2, 39.3, 51.0, 66.7, 75.2, 89.1, 124.4, 126.8, 139.7, 161.8, 166.7, 173.3, 175.1; LR MS m/z 341 (M$^+$); HR FAB MS (M+1) Calcd for $C_{19}H_{20}NO_5$ 342.1341, Found 342.1343.

4.8. Single crystal X-ray diffraction analysis of 3e

Crystal structure data for **3e**: formula $C_{19}H_{19}NO_5$, M=341.36, crystal dimensions 0.50×0.05×0.40 mm, monoclinic, space group $P2_1/n$ (#14), a=13.3182(6) Å, b=6.35582(2) Å, c=19.1422(7) Å, β=102,8125(7)°, V=1579.9(1) Å^3, Z=4, ρ_{calcd}=1.435 g cm^{-3}, $2\theta_{max}$=54.9°, T=93.0 K, R (R_w)=0.035 (0.049) for 2589 reflection data with $I>3.00\sigma(I)$ and 302 variables, GOF=1.21.

4.9. 1f·2 1:1 Complex crystal

A mixture of **1e** (0.50 mmol) and **2** (0.50 mmol) was dissolved in 5 ml of MeCN, and following the same workup as mentioned in the **1d·2** preparation gave **1f·2** (96% yield, mp 75–77°C) as colorless prisms. ^{1}H NMR confirmed a 1:1 ratio of **1f·2**.

4.10. Single crystal X-ray diffraction analysis of 1f·2

Crystal structure data for **1f·2**: formula $C_{18}H_{17}NO_5$, M=327.34, crystal dimensions 0.20×0.20×0.40 mm, orthorhombic, space group $Pnma$ (#62), a=11.2390(3) Å, b=6.6086(2) Å, c=22.8667(7) Å, V=1698.4(2) Å^3, Z=4, ρ_{calcd} 1.280 g cm^{-3}, $2\theta_{max}$=55.0°, T=297.0 K, R (R_w)=0.065 (0.092) for 1392 reflection data with $I>3.00\sigma(I)$ and 140 variables, GOF=1.34.

4.10.1. 11-*p*-Methylbenzyloxy-7-methyl-8-oxa-4-azatricyclo[5.4.0.0^{2,6}]undec-10-en-3,5,9-trione (3f) from the photolysis of 1f·2. Crystals of **1f·2** (164 mg, 0.50 mmol) were sandwiched with two Pyrex glass plates and photolyzed for 24 h. The same workup gave **3f** (147 mg, 90% yield) as colorless plates together with recovery of **1f·2** (3%). Mp 255–258°C; IR (KBr) 1780, 1720, 1710 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 1.59 (3H, s), 2.32 (3H, s), 3.41 (1H, d, J=6.4 Hz), 3.52 (1H, dd, J=6.4, 9.4 Hz), 3.66 (1H, d, J=9.4 Hz), 4.78 (1H, d, J=11.6 Hz), 4.95 (1H, d, J=11.6 Hz), 5.38 (1H, s), 7.21 (2H, d, J=8.0 Hz), 7.31 (2H, d, J=8.0 Hz), 11.48 (1H, s); ^{13}C NMR (DMSO-d$_6$) δ 19.3, 26.1, 39.2, 39.4, 51.1, 69.3, 75.3, 89.8, 126.9, 127.5, 130.4, 136.2, 161.7, 173.3, 175.2; LR MS m/z 327 (M$^+$). Anal. Calcd for $C_{16}H_{17}NO_5$: C, 66.05; H, 5.23; N, 4.28. Found C, 65.42; H, 5.21; N, 4.67.

4.11. Single crystal X-ray diffraction analysis of 3f

Crystal structure data for **3f**: formula $C_{18}H_{17}NO_5$, M=327.34, crystal dimensions 0.50×0.20×0.50 mm, monoclinic, space group $P2_1/n$ (#14), a=7.3266(4)) Å, b=20.745(1) Å, c=10.3288(8) Å, β=105.666(2)°, V=1511.6(2) Å^3, Z=4, ρ_{calcd} 1.438 g cm^{-3}, $2\theta_{max}$=55.0°, T=93.0 K, R (R_w)=0.045 (0.069) for 2806 reflection data with $I>3.00\sigma(I)$ and 286 variables, GOF=1.27.

4.12. 1i·2 1:1 Complex crystal

A mixture of **1i** (0.50 mmol) and **2** (0.50 mmol) was

dissolved in 5 ml of hot CH_2Cl_2, and following the same workup as mentioned in the **1d·2** preparation afforded **1i·2** (96% yield, mp 140–141°C) as colorless plates. ^{1}H NMR confirmed a 1:1 ratio of **1i·2**.

4.13. Single crystal X-ray diffraction analysis of 1i·2

Crystal structure data for **1i·2**: formula $C_{23}H_{19}NO_5$, M=389.41, crystal dimensions 0.08×0.20×0.40 mm, triclinic, space group P-1 (#2), a=11.290(2) Å, b=13.861(1) Å, c=6.2880(7) Å, α=102.420(3)°, β=92.655(5)°, γ=76.000(5)°, V=932.4(2) Å^3, Z=4, ρ_{calcd} 1.387 g cm^{-3}, $2\theta_{max}$=55.0°, T=93.0 K, R (R_w)=0.048 (0.073) for 2925 reflection data with $I>3.00\sigma(I)$ and 391 variables, GOF=1.31.

4.13.1. 11-(4-Biphenylmethyloxy)-7-methyl-8-oxa-4-aza-tricyclo[5.4.0.0^{2,6}]undec-10-en-3,5,9-trione (3i) from the photolysis of 1i·2. Crystals of **1i·2** (117 mg, 0.30 mmol) prepared by method (a) were sandwiched with two Pyrex glass plates and photolyzed for 24 h. The same workup afforded **3i** (61 mg, 52% yield) and recovery of **1i·2** (39%). Similar irradiation to the crystals **1i·2** prepared by method (c), grinded for 30 min gave **3i** (64% yield) together with recovery of **1i·2** (27%). Mp 252–254°C; IR (KBr) 3300, 1765, 1715, 1690 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 1.61 (3H, s), 3.43 (1H, d, J=6.8 Hz), 3.56 (1H, dd, J=6.8, 9.6 Hz), 3.70 (1H, d, J=9.6 Hz), 4.89 (1H, d, J=11.8 Hz), 5.06 (1H, d, J=11.8 Hz), 5.42 (1H, s), 7.3–7.7 (9H, m), 11.49 (1H, s); ^{13}C NMR (DMSO-d$_6$) δ 26.1, 39.2, 39.4, 41.0, 51.1, 69.1, 75.4, 89.9, 125.2, 126.1, 127.4, 132.6, 138.2, 138.7, 161.7, 166.6, 173.3, 175.3, 176.1; LR MS m/z 389 (M$^+$); HR FAB MS (M+1) Calcd for $C_{23}H_{20}NO_5$ 390.1341. Found 390.1342.

4.14. 1j·2 1:1 Complex crystal

A mixture of **1j** (0.50 mmol) and **2** (0.50 mmol) was dissolved in 5 ml of hot CH_2Cl_2, and following the same workup as mentioned in the **1d·2** preparation afforded, using method (a), **1j·2** (95% yield, mp 109–110°C) as colorless plates. ^{1}H NMR confirmed a 1:1 ratio of **1j·2**.

4.15. Single crystal X-ray diffraction analysis of 1j·2

Crystal structure data for **1j·2**: formula $C_{21}H_{17}NO_5$, M=363.37, crystal dimensions 0.10×0.40×0.50 mm, triclinic, space group P-1 (#2), a=10.302(2) Å, b=12.236(2) Å, c=7.6812(9) Å, α=105.095(8)°, β=105.383(7)°, γ=68.270(4)°, V=855.9(2) Å^3, Z=2, ρ_{calcd} 1.410 g cm^{-3}, $2\theta_{max}$=54.9°, T=93.0 K, R (R_w)=0.042 (0.071) for 2421 reflection data with $I>3.00\sigma(I)$ and 312 variables, GOF=1.31.

4.15.1. 11-(1-Naphthylmethyloxy)-7-methyl-8-oxa-4-aza-tricyclo[5.4.0.0^{2,6}]undec-10-en-3,5,9-trione (3j) from the photolysis of 1j·2. Crystals of **1j·2** (182 mg, 0.50 mmol) prepared by method (a) were sandwiched with two Pyrex glass plates and photolyzed for 24 h. The same workup afforded **3j** (118 mg, 65% yield) together with recovery of **1j·2** (25%). Similar irradiation to the crystal **1j·2** (0.30 mmol) prepared by method (c), grinded for 30 min gave **3j** (83% yield) and recovery of **1j·2** (9%). Mp 303–305°C; IR (KBr) 3300, 1767, 1712, 1685 cm^{-1}; ^{1}H NMR (DMSO-d$_6$) δ 1.60 (3H, s), 3.43 (1H, d, J=6.4 Hz), 3.51 (1H, dd, J=6.4, 9.6 Hz), 3.68 (1H, d, J=9.6 Hz), 5.30 (1H, d, J=11.6 Hz), 5.45 (1H, d, J=11.6 Hz), 5.64 (1H, s), 7.5–8.2 (7H, m), 11.52 (1H, s); ^{13}C NMR (DMSO-d$_6$) δ 26.1, 38.7, 39.7, 51.0, 67.7, 75.9, 89.9, 122.7, 123.8, 124.6, 125.1, 126.1, 126.9, 127.3, 129.0, 129.7, 131.7, 161.8, 166.6, 173.3, 175.4; LR MS m/z 363 (M$^+$). Anal. Calcd for $C_{21}H_{17}NO_5$: C, 69.41; H, 4.72; N, 3.85. Found: C, 69.14; H, 4.73; N, 3.87.

4.16. Photoreaction of 1b with 2 in solution

A solution of **1b** (206 mg, 1.0 mmol), **2** (98 mg, 1.0 mmol), and benzophenone (73 mg, 0.40 mmol) in MeCN (30 ml) was irradiated for 5 h under nitrogen atmosphere at room temperature. After evaporating the solvent, the resulting residue was submitted to column chromatography (silica gel, ethyl acetate–hexane=1:1) to give a mixture of **3b** (10% yield) and **5b** (12% yield) whose yields were obtained from ^{1}H NMR analysis, together with unidentified compounds. **5b**: ^{1}H NMR (DMSO-d$_6$) δ 1.65 (3H, s), 2.59 (1H, d, J=8.0 Hz), 2.64 (1H, d, J=9.6 Hz), 2.84 (1H, dd, J=3.2, 8.0 Hz), 2.97 (1H, m), 3.07 (1H, dd, J=3.2, 9.6 Hz), 4.54 (1H, s), 4.59 (1H, d, J=12.4 Hz), 4.66 (1H, d, J=12.4 Hz), 6.33 (1H, d, J=2.8 Hz), 6.38 (1H, m), 7.60 (1H, m), 11.20 (1H, s), 11.36 (1H, s).

4.17. Photoreaction of 1d with 2 in solution

Similar photoirradiation to a solution of **1d** (217 mg, 1.0 mmol), **2** (98 mg, 1.0 mmol), and benzophenone (74 mg, 0.41 mmol) in MeCN (40 ml), and same workup afforded a mixture of **3d** (10% yield) and **5d** (18% yield) (^{1}H NMR analysis) together with unidentified compounds. **5d**: ^{1}H NMR (DMSO-d$_6$) δ 1.63 (3H, s), 2.60 (1H, d, J=8.0 Hz), 2.64 (1H, d, J=9.6 Hz), 2.88 (1H, dd, J=2.8, 8.0 Hz), 3.06 (1H, m), 3.15 (1H, dd, J=3.6, 9.6 Hz), 4.64 (1H, d, J=12.4 Hz), 4.72 (1H, s), 4.76 (1H, d, J=12.4 Hz), 7.2–7.5 (5H, m), 11.21 (1H, s), 11.36 (1H, s).

4.18. Photoreaction of 1i with 2 in solution

Similar photoirradiation to a solution of **1i** (586 mg, 2.0 mmol), **2** (195 mg, 2.0 mmol), and benzophenone (158 mg, 0.87 mmol) in MeCN (60 ml), and same workup afforded a mixture of **3i** (9% yield) and **5i** (13% yield) (^{1}H NMR analysis) together with unidentified compounds. **5i**: ^{1}H NMR (DMSO-d$_6$) δ 1.64 (3H, s), 2.60 (1H, d, J=8.0 Hz), 2.65 (1H, d, J=9.4 Hz), 2.90 (1H, dd, J=2.8, 8.0 Hz), 3.09 (1H, m), 3.16 (1H, dd, J=7.0, 9.4 Hz), 4.70 (1H, d, J=12.4 Hz), 4.74 (1H, s), 4.82 (1H, d, J=12.4 Hz), 7.4–7.7 (9H, m), 11.23 (1H, s), 11.37 (1H, s).

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