Peri-, Site- and Stereocontrolled Photocycloaddition of 4-Methoxy-6-methyl-2-pyrone with Maleimide Induced by the Hydrogen Bond and CT Stacking in the Solid State

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Photoirradiation of a 1:1 complex crystal of 4-methoxy-6-methyl-2-pyrone (**1**) with maleimide (**2**) peri-, site- and stereospecifically gave 11-methoxy-7-methyl-4-aza-8-oxatricyclo [5.4.0.0^{2,6}]undec-10-en-3,5,9-trione (**3**) (*endo*-[2+2]adduct), which was different from the solution products. It was inferred to be effectively brought by two sets of the hydrogen bonding and CT stacking between **1** and **2**.

Photochemical reactions in the solid state afford uncommon and interesting results because molecules are disposed tightly and regularly in the environment.[1-3] Although much attention has been denoted to the [2+2]photodimerization reactions in the crystals,[1,4] a little investigation of intermolecular [2+2] cycloaddition reactions between two different organic molecules has been reported.[5] In this communication we describe the solid state and comparative solution phase photocycloaddition reactions of **1** with **2**. They demonstrate that hydrogen bonding and CT stacking can be used to compel a particular and desirable peri-, site- and stereochemical [2+2]cycloaddition in the solid state photoreaction.

Irradiation of a 1:1 complex crystal (mp 95 - 97 ℃, plates) between **1** (mp 84 - 87 ℃) and **2** (mp 92 - 94 ℃), which was prepared by recrystallization of the equimolecular substrates from acetonitrile, with a 400 W high-pressure mercury lamp through a Pyrex filter under nitrogen at room temperature gave [2+2]cycloadduct **3** in 54% yield as a sole product (Scheme 1). The structure of **3** was determined by X-ray crystallographic analysis as being 11-methoxy-7-methyl-4-aza-8-oxatricyclo [5.4.0.0^{2,6}]undec-10-en-3,5,9-trione (*endo* adduct).[6] The photochemical behavior can be readily interpreted by X-ray structure analysis of the 1:1 complex crystal between **1** and **2** as shown in Figure 1.[7] The molecule **1** is connected to another molecule **2** in the hydrogen bonding through those O–C=O··· HN with the O···H distance of 1.83 Å from the molecular packing of the 1:1 complex crystal, which has higher melting point than each substrate. The intermolecular distances of two facing double bonds between **1** and **2** are 3.63 Å (C(6)···C(13))

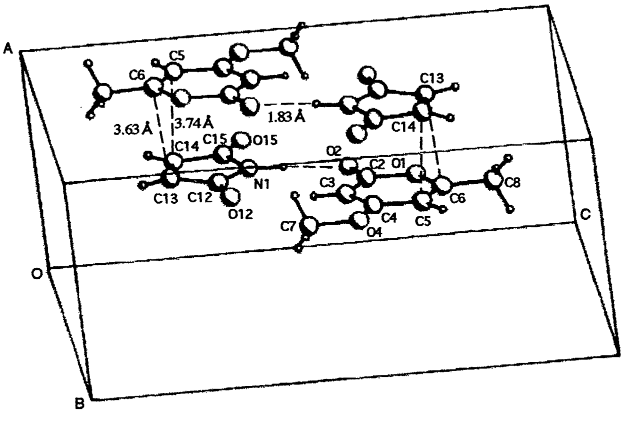
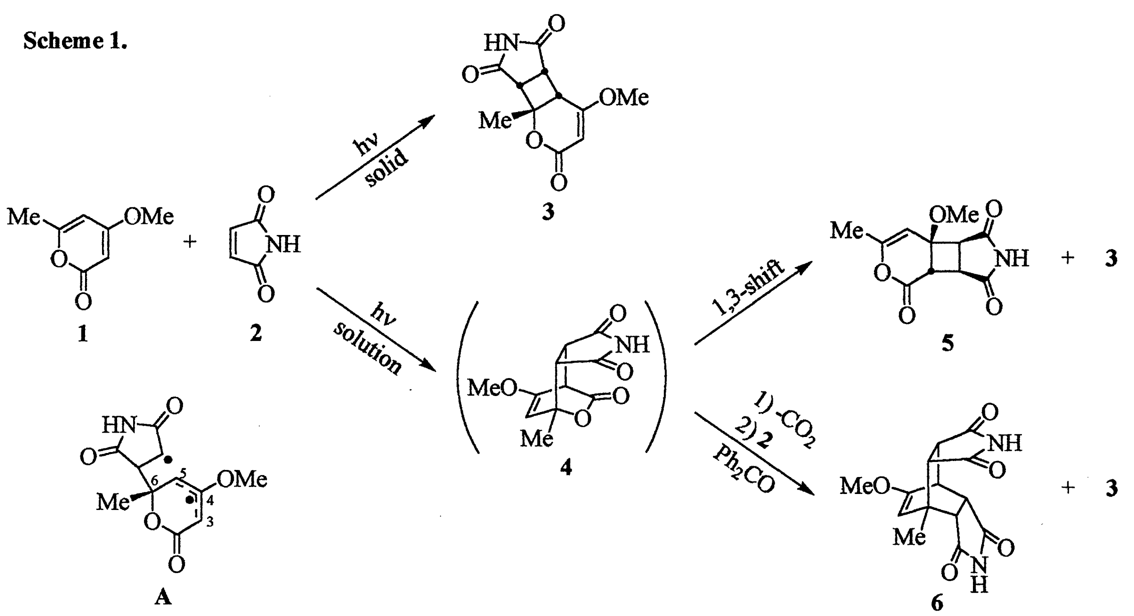


Figure 1. Molecular packing in the 1:1 complex crystal of **1** with **2**.

Scheme 1.



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and 3.74 Å (C(5)···C(14)) which are within the normal photoreaction distance in the solid state.[8] Such crystal structure is inferred to be effectively brought by two sets of the O-C=O··· HN hydrogen bondings and CT stackings between **1** and **2** as shown in Figure 1. Such electrostatic property was appeared at our previous report.[10a] Since similar solid state photoreactions of **1** with *N*-methylmaleimide and *N*-phenylmaleimide, whose mixture gave lower melting points than each substrate, gave no cycloadduct, the existence of C=O···HN hydrogen bonding is also found to be necessary to the [2+2]cycloaddition in addition to the CT stacking in this system. Compound **3** was also obtained in 33% yield from irradiation of the 1:1 complex crystal which was prepared by removal of solvent from equimolar ethanol solution of **1** and **2**.

Direct photoirradiation to an acetonitrile solution of **1** and **2** gave another type of [2+2]cycloadduct **5** in 25% yield together with a small amount of cycloadduct **3**. The structure of **5** was assigned as 1-methoxy-10-methyl-4-aza-9-oxatricyclo[5.4.0.0^{2,6}]undec-10-en-3,5,8-trione from the spectral data and the stereochemistry was confirmed by the ^{1}H NMR NOE measurement.[9] On the other hand, sensitized photoreaction of **1** with **2** gave bis-adduct **6** which was formed through decarboxylation of the [4+2]cycloadduct **4** followed by addition of another molecule of **2**.[10] The *exo-endo* configuration of **6** was assumed by inspection of the ^{1}H NMR spectral data in comparison with that of the *endo-endo* bis-adduct, which was obtained from the thermal reaction. They have different 2- and 6-H chemical shifts by shielding effect of the C=C double bonds.[10b]

The photoreaction intermediate of **3**, **5**, and **6**, can be estimated to biradical **A** by frontier MO analysis.[10a] It was inferred that the intermediate **A** was enough close to react at the 5-position of **A** to give product **3** in the solid state, on the other hand, solution reactions gave **5** and **6** via **4** in addition to **3** (Scheme 1).

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7 X-ray crystallographic analysis was carried out on a ENRAF NONIUS FR590 diffractometer. The diffraction data were collected with the use of MoKα radiation and 755 independent reflactions were used for solving the structure by the CAD4 program. All non-H atoms were located by direct methods using SIR88 and refined anisotropically. Positional parameters of H atoms were calculated from the positions of C and N, and not refined. Crystal data for the 1:1 complex crystal of **1** with **2**: $C_{11}H_{11}NO_5$, formula weight=237.21, monoclinic space group $P2_1/n$, a=6.678(2) Å, b=11.354(2) Å, c=15.105(4) Å, V=1141.8 Å^3, Z=4, d_{calc}=1.38 gcm^{-3}, $R(R_w)$= 0.075(0.095) for 755 reflection data with $I>3\sigma(I)$ and 154 variables.

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9 All the new compounds gave the correct analytical and MS data. Selected NMR spectral data are given below: **3**, ^{1}H NMR (400 MHz, DMSO-d_6): 1.58 (3H, s), 3.41 (1H, d, J=6.8 Hz), 3.51 (1H, dd, J=6.8, 9.2 Hz), 3.63 (1H, d, J=9.2 Hz), 3.67 (3H, s), 5.26 (1H, s), 11.43 (1H, s) ; **5**, ^{1}H NMR (400 MHz, DMSO-d_6): 1.96 (3H, s), 3.08 (3H, s), 3.27 (1H, dd, J=5.6, 12.0 Hz), 3.32 (1H, d, J=12.0 Hz), 3.46 (1H, d, J=5.6 Hz), 5.26 (1H, s), 11.44 (1H, s); **6**, ^{1}H NMR (400 MHz, DMSO-d_6): 1.63 (3H, s), 2.58 (1H, d, J=8.0 Hz), 2.62 (1H, d, J=9.6 Hz), 2.84 (1H, dd, J=2.8, 8.0 Hz), 2.98 (1H, dd, J=2.8, 4.4 Hz), 3.09 (1H, dd, J=4.4, 9.6 Hz), 3.42 (3H, s), 4.62 (1H, s), 11.19 (1H, s), 11.35 (1H, s).

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