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Photochemistry of 2-(3,4,5-Trimethoxyphenyl)-4-(3,4-methylenedioxyphenyl)-4-oxo-2-butenonitrile (β-Cyanochalcone) and Its Related Compounds

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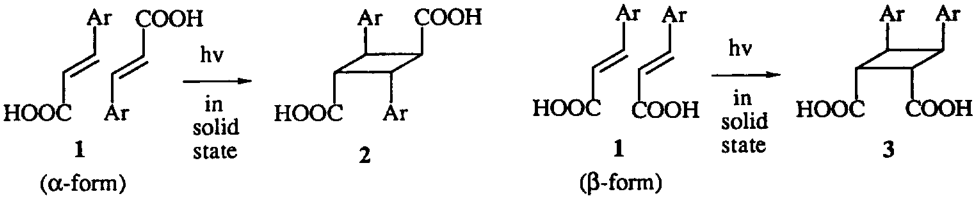
Abstract: Photochemistry of the titled compounds both in solid state and in solution is described. The (*Z*)-isomers of β-substituted chalcones (**5**, **8** and **9**) mainly dimerized into topochemically favored single cyclobutane dimers (**10**, **14** and **13**) in solid state photoreactions, while in solution those isomerized into the corresponding (*E*)-isomers. Interestingly exposure of the (*E*)-isomer (**5E**) of β-cyanochalcone to sunlight in the solid state led to unusual dimerization through isomerization to give an unsymmetrical (*E*-*Z*)-dimer (**11**) along with a symmetrical (*Z*-*Z*)-dimer (**10**) obtainable from the photoreactive (*Z*)-isomer (**5Z-b**). The photochemical reactivities of the esters (**9**) are discussed based on their crystal structures.

INTRODUCTION

In solid state photoreactions[1] of alkenic compounds most of dimerization are strictly controlled by the topochemistry to give single dimers and the reactive partners must be within a distance of *ca.* 4.2 Å. It is well known that among trimorphic forms of the crystals of (*E*)-*o*-ethoxycinnamic acid (**1**) the α-form crystal transformed into an α-truxillic acid (**2**) ($\bar{1}$-dimer) and the β-one into a β-truxinic acid (**3**) (m-dimer) on irradiation of light, while the γ-one was inert to light.[2] (Scheme 1) We preliminarily reported an anomalous photobehaviors[3] of the (*E*)-isomer (**5E**) of 2-(3,4,5-trimethoxyphenyl)-4-(3,4-methylenedioxyphenyl)-4-oxo-2-butenonitrile (β-cyanochalcone) in solid state, which led to formation of unexpected dimers (**10** and



Ar=*o*-ethoxyphenyl

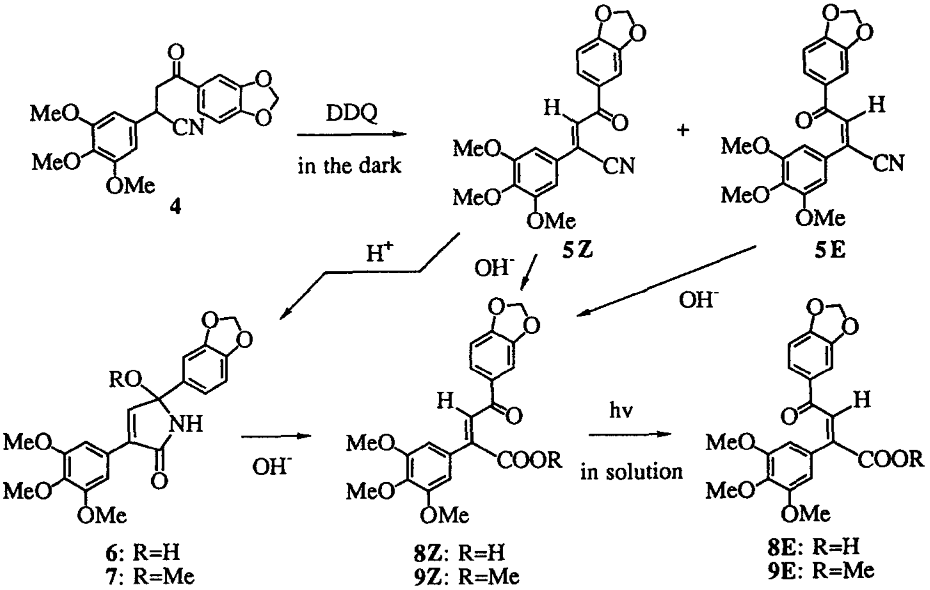
Scheme 1

11) through isomerization when exposed to sunlight. This paper describes the photochemistry of **5** and its related β-substituted chalcones (**8** and **9**) in details.

RESULTS AND DISCUSSION

Preparation of β-Substituted Chalcones

Each geometrical isomer (**5E** and **5Z**) of β-cyanochalcones were prepared by dehydrogenation of the saturated nitrile[4] (**4**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in the dark in 40.2 % and 44.4 % yields, respectively. (Scheme 2) Their stereochemistries were confirmed by difference NOE experiments in their ^{1}H-NMR spectra. In the (*E*)-isomer (**5E**) irradiation of the signal at δ 7.13, due to an olefinic proton, enhanced the integrals of both aromatic protons at *ortho* positions in the methylenedioxybenzoyl group. But in the (Z)-isomer (**5Z**) an additional NOE enhancement was observed between the aromatic protons in the trimethoxyphenyl group and an olefinic proton.

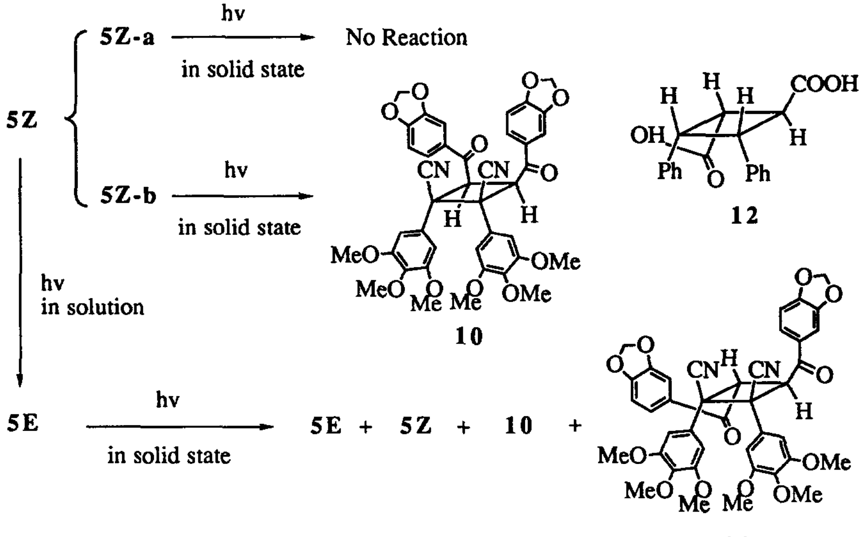


Scheme 2

Acid hydrolysis of the (Z)-nitrile (**5Z**) gave a hydroxypyrrolidone (**6**) as a single product. It was easily converted into the corresponding methyl ether (**7**) by heating in methanol (MeOH) in the presence of acid. Alkaline hydrolysis of **6** yielded the (Z)-acid (**8Z**) in 87 % yield, which could be also afforded in high yield by direct alkaline hydrolysis of **5Z**. Contrastly acid hydrolysis of the (*E*)-nitrile (**5E**) resulted in recovery of the starting material and the alkaline hydrolysis in exclusive formation of **8Z** through isomerization. The (*E*)-acid (**8E**) was quantitatively obtainable by photoisomerization of **8Z** in solution. Esterification of each isomeric acid (**8**) with diazomethane smoothly gave the corresponding methyl ester (**9**) without isomerization. The (Z)-ester (**9Z**), like the (Z)-acid (**8Z**), photochemically isomerized to the (*E*)-ester (**9E**) (*vide infra*). (Scheme 2) Stereochemical assignment of the structures of unsaturated acids (**8**) and esters (**9**) was based on the same criteria as that of the nitriles (**5**).

Photoreactions of the Chalcones

The (Z)-isomer (**5Z**) of the nitrile was crystallized into dimorphic forms [**5Z-a**: yellow fine prisms, mp 153-156 °C; **5Z-b**: yellow fine needles, mp 168-169.5 °C]. Though the crystal (**5Z-a**) with a lower melting point was found to be quite stable to light, the other crystal (**5Z-b**) smoothly underwent solid state photoreaction to yield colorless needles (**10**), mp 169-170 °C[5], as a sole isolable product (70.2 %). (Scheme 3) Heating a solution of **10** in ethyl acetate (AcOEt) completely gave the corresponding monomer (**5Z**). Such easy thermal regeneration of **5Z** from **10** suggested that **10** was a symmetrical cyclobutane dimer derived from **5Z**. This was supported by its ^{1}H-NMR spectrum showing only one singlet at δ 4.88 due to a newly born methine proton in place of the disappearance of an olefinic proton. The mirror symmetry structure of **10** was established by X-ray crystallographic analysis (Fig. 1),



Scheme 3

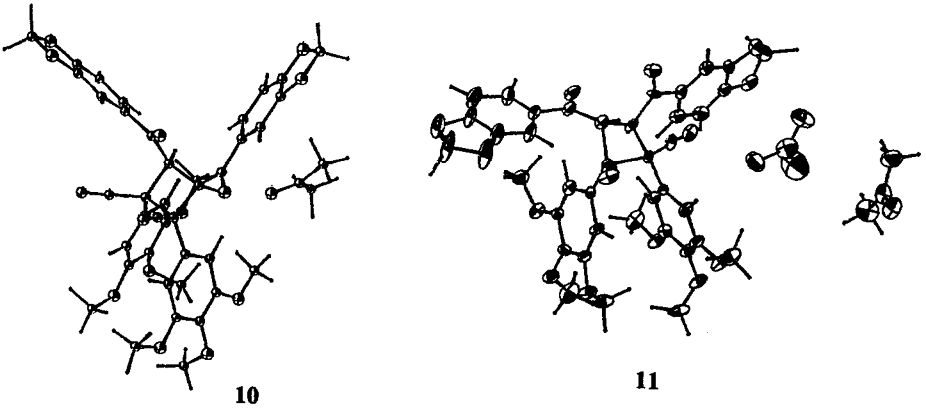
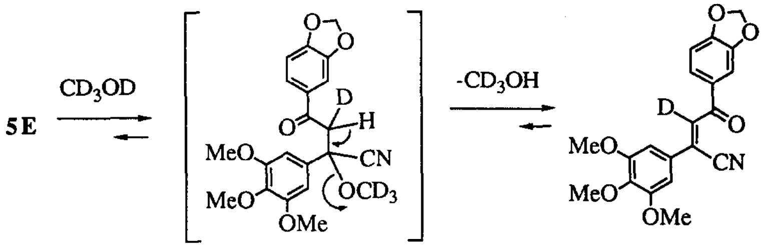


Fig. 1. ORTEP drawing of dimers (10 and 11)

strongly suggesting that the starting **5Z-b**[6] crystallizes in the β-modification responsible for topochemical translation to a mirror symmetry dimer such as a β-truxinic acid (3).

Exposure of the (*E*)-isomer (**5E**) to sunlight or Daylight lamp® for 37.5 h afforded two dimers along with the starting **5E** (33.7 %) and the isomerized **5Z** (27.7 %) monomers. (Scheme 3) One of the dimers yielded in 11.0 % was identified as the same symmetrical dimer (**10**) that was derived from the photoreactive (*Z*)-isomer (**5Z-b**). The second dimer (**11**) was given as colorless fine needles, mp 117-120 °C, in 14.6 % yield. Thermal generation of the isomeric monomers (**5E** and **5Z**) from this dimer (**11**) and isomerization of the symmetrical dimer (**10**) to the alternative dimer (**11**) by silica gel suggested that **11** belonged to an unsymmetrical (*E*-*Z*)-dimer with the configuration of *neo*-truxinic acid (**12**).[7] The ^{1}H-NMR spectrum showed coupled 1H doublets (J=10.4 Hz) at δ 5.34 and δ 5.44 attributable to newly born methine protons. NOE enhancements was observed between the methine proton at δ 5.34 and four aromatic protons at *ortho* positions of two trimethoxyphenyl rings. Thus we could depict a chiral structure as **11** for the second dimer. The correctness of the structure was unambiguously confirmed by X-ray crystallographic analysis. (Fig. 1)

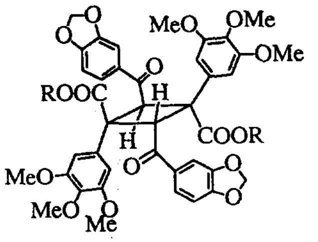
As a comparable experiment we examined the photochemistry of the nitrile (**5**) in solution. Irradiation of each isomer (**5E** and **5Z**) led to nearly quantitative isolation of **5E**, indicating that a photosensitive **5E** in solid state existed as a photostable isomer in solution. Interestingly, the (*E*)-nitrile (**5E**) was observed to thermally isomerize to **5Z** when heated in MeOH under protection of light. In equilibrium a ratio of the (*E*)- to the (*Z*)-isomer was *ca.* 35 : 65. This thermal isomerization could not be observed in other solvents such as benzene (even if containing *p*-TsOH) and AcOEt, suggesting that MeOH would catalyze the isomerization. When **5E** was heated in deuteriomethanol (CD_3OD), substitution of an olefinic proton to a deuterium was observed. These facts suggested that the isomerization should be caused by Michael type addition of CD_3OD followed by elimination of CD_3OH due to isotope effect as shown in Scheme 4.



Scheme 4

The solid state photoreaction of the (*Z*)-ester (**9Z**) with Daylight lamp® gave the isomerized **9E** and a dimerized product (**13**) in 16.1 % and 52.7 % yields, respectively, along with recovery of the starting **9Z** (13.9 %). The spectral data of **13**, particularly the ^{1}H-NMR spectrum, allowed us to deduce it as a symmetrical dimer and finally a ī-dimer structure for it such as an α–truxillic acid (**2**) was unambiguously established by X-ray crystallographic analysis. (Fig. 2) On the other hand the (*E*)-ester (**9E**) was stable to light both in solid state and in solution.

Each isomer of the acids (**8**) showed a similar photobehavior to the corresponding ester (**9**) in both states. The structure of a dimer (**14**) formed in the solid state reaction of **8Z** was confirmed by chemical conversion to the ester dimer (**13**) by methylation with diazomethane. Though the (*E*)-acid (**8E**) was crystallized into tetramorphic forms with close melting points [**8E-a**: pale yellow fine needles, mp 194-198 °C; **8E-b**: yellow fine needles, mp 198-200 °C; **8E-c**: colorless fine needles, mp 194-198 °C; **8E-d**: pale yellow fine needles, mp 199-202 °C], all of the crystals were found to be inert to light.



13: R=Me
14: R=H

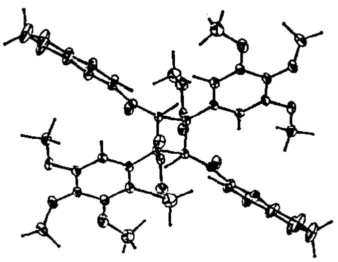


Fig. 2. ORTEP drawing of **13**

Quantitative Analysis of the Photoreactions by HPLC

Photoreactions of the β-substituted chalcones were traced by HPLC. (The conditions: see **Experimental**) In the solid state reaction of **5E** the (*E*-*Z*)-dimer (**11**) was immediately detected after isomerization started while formation of the (Z-Z)-dimer (**10**) was much slower (after *ca.* 4 h). (Fig. 3) In the case of **5Z-b** isomerization to **5E** was observed as a minor path though **5E** could not be obtained in the isolation work. (Fig. 4)

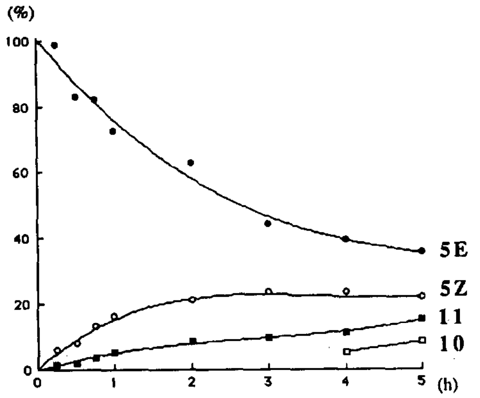


Fig. 3. HPLC analysis of the solid state photoreaction of **5E**

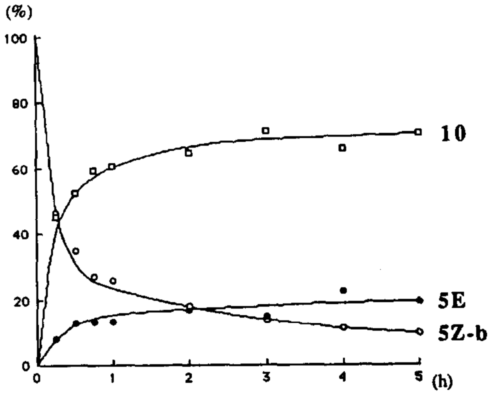


Fig. 4. HPLC analysis of the solid state photoreaction of **5Z-b**

In the liquid phase photostationary state a proportion of **5E** in the equilibrium mixture reached to *ca.* 95 %. (Table 1) The UV spectrum of **5Z** in AcOEt showed an absorption maximum at 364 nm while that of **5E** at 322 nm in the longest wave length region and the intensity was greater in the former (log ε 4.22) than in the latter (log ε 4.07). As these UV data showed more effective absorption of sunlight by **5Z** than **5E**, the photobehavior of **5** in solution could be reasonably explained.

Smooth isomerization and dimerization were also observed in the solid state photoreaction of the (*Z*)-ester (**9Z**) like **5Z-b** (Fig. 5) and in solution **9E** was found to be quite stable to light. (Table 1)

On the acid (**8**) only the reaction in solution was traced by HPLC. After irradiation in three different kinds of solvents (MeOH, acetone and AcOEt) the product mixture in the photostationary state was analyzed. (Table 1) In more polar solvents such as MeOH or acetone the proportion of the (*E*)-isomer (**8E**) was over 92 %, while that in less polar AcOEt was decreased to 76 %. The UV spectrum of each isomer in MeOH [λ_{max} (log ε): 322 (3.97) in **8E**; 339 (4.23) in **8Z**] supported the photobehavior

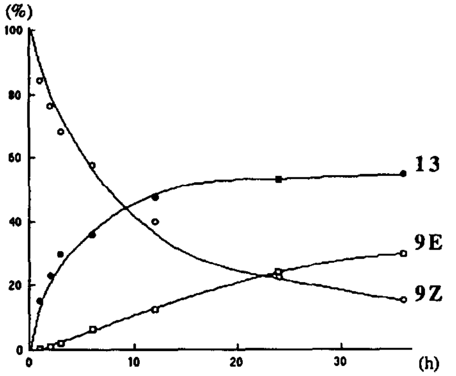
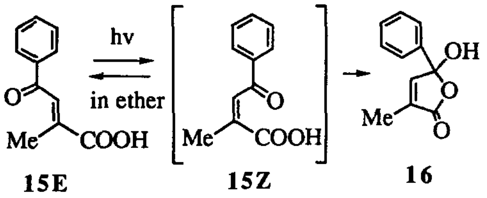


Fig. 5. HPLC analysis of the solid state photoreaction of **9Z**

Table 1. Proportion of *E*/*Z*-Isomers in Liquid Phase Photostationary State

Starting materials	Irradiation time (h)	Solvents	Products E	Products Z
5	6	MeOH	94	6
		AcOEt	96	4
8	18	MeOH	96	4
		Acetone	92	8
		AcOEt	76	24
9	6	MeOH	99	1



Scheme 5

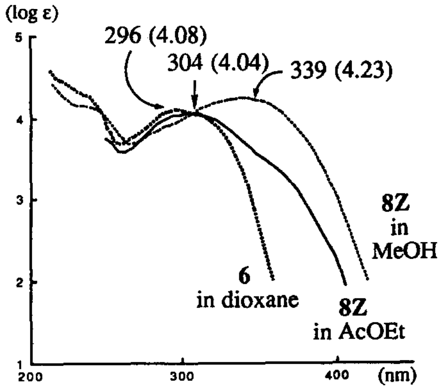
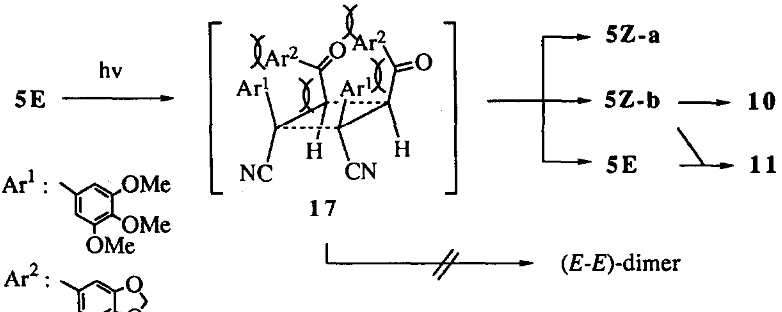


Fig. 6. UV spectra of **8Z** and **6**

of **8** in more polar solvents as mentioned above. However a remarkable blue shift in the UV spectrum of **8Z** was observed when measured in AcOEt. It has been reported that (*E*)-3-benzoyl-2-methylacrylic acid[8] (**15E**) photochemically falls in equilibrium to a cyclic tautomer (**16**) of the (*Z*)-isomer (**15Z**) in ether. (Scheme 5) Comparison of the UV spectrum of **8Z** in AcOEt with that of the pyrrolidone (**6**) in dioxane suggested the larger proportion of a cyclic tautomer such as **16** in the equilibrium mixture in AcOEt than in MeOH. (Fig. 6) This was also supported by appearance of an IR absorption band in chloroform solution at 1770 cm^{-1} due to a carbonyl group in the butenolide structure. Thus, we could safely conclude that the higher proportion of **8Z** in AcOEt than in MeOH or acetone under the condition of photoequilibrium was attributable to its ability to cyclize intramolecularly in a less polar solvent.

CONCLUSION

Sunlight irradiation of the (*E*)-nitrile (**5E**) in solid state preferentially induced isomerization followed by dimerization. Solid state photoisomerization of alkenic compounds is not so common as dimerization. A lattice-controlled isomerization through a metastable complex has been proposed as one of possible mechanisms for solid state photoisomerization[9] and more recently an importance of a disordered crystal structure of the starting monomer for the photoisomerization has been pointed out.[10] Unfortunately trials to prepare a single crystal of **5E** for X-ray analysis have not been successful, but the formation[11] of the dimers (**10** and **11**) suggested that the starting **5E** crystallized in β-modification. Though precise discussion on the solid state photochemistry[12] of **5E** has failed because of lack of the



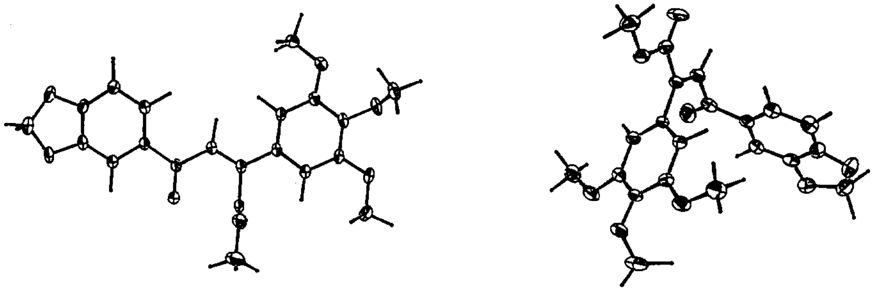
Scheme 6

crystal data of **5E**, three-dimensional studies of the supposed metastable complex[9] (**17**) using a Dreiding model shows that direct [2+2] cycloaddition from the complex (**17**) would be impossible due to a severe steric repulsion by the *cis* arrangement of all of the bulky trimethoxyphenyl and the methylenedioxybenzoyl substituents in a formed dimer, even if the dimerization is topochemically favored. (Scheme 6) Thus, in our case the steric restriction effect may also trigger generation of possible monomers (**5E**, **5Z-a** and **5Z-b**) with partial isomerization, the photoreactive (*Z*)-isomer (**5Z-b**) among which could react with either another **5Z-b** or **5E** to produce the [2+2] cycloadducts (**10** and **11**).

Solid state photoreactions of esters (**9**) were deduced by their crystal structures. The X-ray analyses indicated that a photoreactive **9Z** was a planar structure while a photostable **9E** a bended one. (Table 2 and Fig. 7) In **9Z** two molecules are packed in a unit cell (Fig. 8) and they were located with centrosymmetrical head to tail arrangement. The calculated distances (5.70 Å in Cβ-Cα' and 5.69 Å in Cα-Cβ') between the closest olefinic double bonds, which could contribute to photoreaction, are longer than a range of the allowed distance (*ca.* 4.2 Å) of solid state photoreaction under topochemical principle. (Table 3) The torsion angles of Cβ'-Cβ-Cα-Cα' and Cα-Cβ-Cβ'-Cα' were calculated as 11.2° and -132.4°, respectively. Thus though **9Z** was expected to be inert to light because of too long double bond separation, exceptional formation[13] of a dimer (**13**) controlled by the crystal structure of the starting monomer (**9Z**) may suggest possibility of alternative overlap[14] between π electrons causing by molecular

Table 2. Crystal Data of 9 with Standard Deviations in Parentheses

	9Z	9E
Chemical formula	$C_{21}H_{20}O_8$ x 2	$C_{21}H_{20}O_8$
Formula weight	400.00 x 2	400.00
Crystal system	triclinic	monoclinic
Space group	P $\bar{1}$	P 2_1/n
Cell dimensions	a=15.011(33) (Å)	a=9.914(1) (Å)
	b=11.049(12) (Å)	b=6.260(1) (Å)
	c=12.446(31) (Å)	c=32.056(1) (Å)
	α=92.53(1)°	
	β=106.73(1)°	β=103.20(1)°
	γ=74.88(1)°	
Cell volume (Å^3)	1907.64	1936.83
Z value	2 (2 mols/nuit cell)	4
D_c (gcm^{-3})	1.394	1.373



9Z **9E**

Fig. 7. ORTEP drawings of **9**

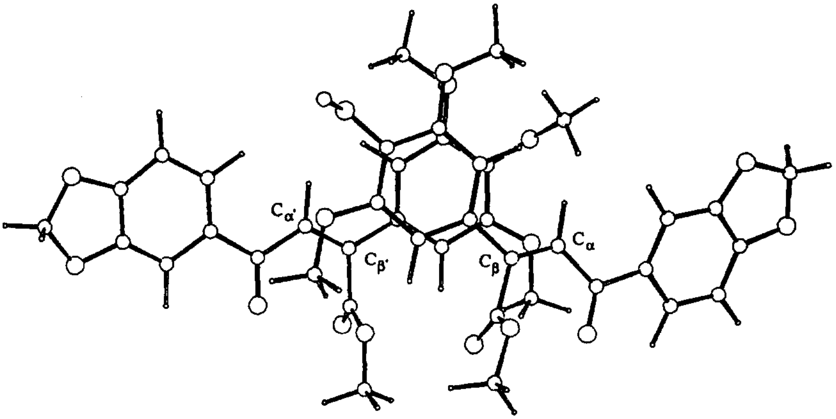


Fig. 8. Molecules of **9Z** in unit cell

Table 3. Selected Bond Distances, Bond Angles and Torsion Angles between Two Molecules of **9Z**

(a) Selected bond distances (Å)

C_{β}-$C_{\beta'}$	4.82
C_{β}-$C_{\alpha'}$	5.70
C_{α}-$C_{\beta'}$	5.69
C_{α}-$C_{\alpha'}$	6.67

(b) Selected bond angles (°)

C_{α}-C_{β}-$C_{\beta'}$	125.3	C_{β}-$C_{\beta'}$-C_{α}	11.1
C_{α}-C_{β}-$C_{\alpha'}$	132.3	C_{β}-$C_{\beta'}$-$C_{\alpha'}$	124.8
$C_{\beta'}$-C_{β}-$C_{\alpha'}$	11.3	C_{α}-$C_{\beta'}$-$C_{\alpha'}$	131.7
C_{β}-C_{α}-$C_{\beta'}$	43.7	C_{β}-$C_{\alpha'}$-C_{α}	8.5
C_{β}-C_{α}-$C_{\alpha'}$	39.2	C_{β}-$C_{\alpha'}$-$C_{\beta'}$	44.0
$C_{\beta'}$-C_{α}-$C_{\alpha'}$	8.7	C_{α}-$C_{\alpha'}$-$C_{\beta'}$	39.6

(c) Selected torsion angles (°)

$C_{\beta'}$-C_{β}-C_{α}-$C_{\alpha'}$	11.2
C_{α}-C_{β}-$C_{\beta'}$-$C_{\alpha'}$	-132.4
C_{α}-C_{β}-$C_{\alpha'}$-$C_{\beta'}$	54.7
C_{β}-C_{α}-$C_{\beta'}$-$C_{\alpha'}$	54.4
C_{β}-C_{α}-$C_{\alpha'}$-$C_{\beta'}$	117.2
C_{β}-$C_{\beta'}$-$C_{\alpha'}$-C_{α}	10.9

distortion in an excited state in addition to the traditional double bond separation.

EXPERIMENTAL

All melting points were measured on a micro melting point hot-stage apparatus (Yanagimoto) and are uncorrected. IR spectra were recorded for Nujol mulls on a Hitachi 260-10 and UV spectra on a Hitachi U-3400 spectrophotometers, respectively. Shoulder peaks are abbreviated as sh. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ solution with a JOEL JNM FX- or GX-270, JNM GSX-400 or JNM GSX-500 spectrometers, unless otherwise stated, with tetramethylsilane as an internal reference. Peak multiplicities are quoted in Hz. Diffused and broad splitting patterns are abbreviated as dif and br, respectively. MS were measured with a Hitachi M-60 (EI mode), Hitachi RMU-7M (HR mode), or a JOEL JMS-HX-110A (EI and FAB modes) spectrometers. For matrix in FABMS was used *m*-nitrobenzyl alcohol. For column chromatography silica gel 60 (70-230 mesh, Merck) and for TLC DC-Fertigplatten SIL G-25 UV254 (Macherey-Nagel) were used. All the measurements for X-ray crystallographic studies were performed on a Rigaku Denki AFC-5 automatic four-circle diffractometer using CuK$_\alpha$ radiation. The structure was solved by the direct method with MULTAN 80 program and refined by the full-matrix least-squares method. X-ray powder diffraction patterns were recorded using a Rigaku Denki 2027 diffractometer. For the HPLC system JASCO 880-PU was used as a pump unit, JASCO UVIDEC-100-V as a detector and JASCO RC-250 as a recorder. For a column cosmosil 5SL (4.6 x 250 mm, Nacalai) was used. Solid state photochemical reactions were carried out using powdered starting materials spread in a PYREX® petridish or put between PYREX® glass plates by either exposure to sunlight or irradiation with Daylight lamp® DR250/T(L) (Toshiba) with a 2.5MT-103H-A as a stabilizer in the dark at ambient temperature.

Dehydrogenation of the Saturated Nitrile (4) A solution of **4** (5.00 g, 13.6 mmol) and DDQ (9.23 g, 40.7 mmol) in abs. benzene (267 ml) was refluxed for 18.5 h in the dark under Ar. After removal of the precipitates by filtration the filtrate was evaporated. The residue (12.4 g) was purified by column chromatography with benzene followed by AcOEt-benzene (40 : 3, v/v).

i) (*E*)-2-(3,4,5-Trimethoxyphenyl)-4-(3,4-methylenedioxyphenyl)-4-oxobutenonitrile (**5E**): Recrystallization of the less polar component from benzene-hexane afforded yellow fine needles (2.00 g, 40.2%), mp 112-114 °C. *Anal.* Calcd for $C_{20}H_{17}NO_6$: C, 65.39; H, 4.66; N, 3.81. Found: C, 65.39; H, 4.72; N, 3.78. IR cm^{-1}: 2225, 1650. UV nm (log ε) (EtOH): 232 (4.29)sh, 274 (3.97), 326 (4.05); (AcOEt): 272 (3.97), 322 (4.07). ^{1}H-NMR (270 MHz) δ: 3.74 (6H, s, $C_{3''}$- and $C_{5''}$-OCH_3), 3.81 (3H, s, $C_{4''}$-OCH_3), 6.06 (2H, s, OCH_2O), 6.65 (2H, s, $C_{2''}$- and $C_{6''}$-H), 6.81 (1H, d, *J*=8.2 Hz, $C_{5'}$-H), 7.13 (1H, s, C_3-H), 7.36 (1H, d, *J*=1.5 Hz, $C_{2'}$-H), 7.46 (1H, dd, *J*=8.2, 1.5 Hz, $C_{6'}$-H). ^{13}C-NMR (67.8 MHz) δ: 56.1 (q, $C_{3''}$- and $C_{5''}$-OCH_3), 60.9 (q, $C_{4''}$-OCH_3), 102.3 (t, OCH_2O), 105.9 (d, $C_{2''}$ and $C_{6''}$), 107.7 (d, $C_{2'}$ and $C_{5'}$), 117.9 (s, CN), 121.5 (s, $C_{1'}$ or $C_{4''}$), 126.4 (s, $C_{4''}$ or $C_{1'}$), 126.5 (d, $C_{6'}$), 130.2 (s, $C_{1''}$), 139.2 (d, C_3), 139.7 (s, C_2), 148.8 (s, $C_{3'}$ and $C_{4'}$), 153.2 (s, $C_{3''}$ and $C_{5''}$), 190.3 (s, CO). EIMS *m/z*: 367 (M^+, 84.7%), 336 (M^+-OMe, 100%).

ii) (*Z*)-2-(3,4,5-Trimethoxyphenyl)-3-(3,4-methylenedioxyphenyl)-4-oxobutenonitrile (**5Z-a**):

Recrystallization of the more polar component from benzene-hexane afforded yellow fine prisms (2.21 g, 44.4%), mp 153-156 °C. *Anal.* Calcd for $C_{20}H_{17}NO_6$: C, 65.39; H, 4.66; N, 3.81. Found: C, 65.23; H, 4.47; N, 3.51. IR cm^{-1} (KBr): 2225, 1650; ($CHCl_3$): 1660. UV nm (log ε) (EtOH): 238 (4.16)sh, 266 (4.00)sh, 358 (4.09); (AcOEt): 364 (4.22). ^{1}H-NMR (270 MHz) δ: 3.92 (3H, s, $C_{4''}$-OCH_3), 3.95 (6H, s, $C_{3''}$- and $C_{5''}$-OCH_3), 6.09 (2H, s, OCH_2O), 6.91 (1H, d, *J*=7.9 Hz, $C_{5'}$-H), 6.99 (2H, s, $C_{2''}$- and $C_{6''}$-H), 7.52 (1H, d, *J*=1.8 Hz, $C_{2'}$-H), 7.61 (1H, dd, *J*=7.9, 1.8 Hz, $C_{6'}$-H), 7.13 (1H, s, C_3-H). ^{13}C-NMR (67.5 MHz) δ: 56.4 (q, $C_{3''}$- and $C_{5''}$-OCH_3), 61.1 (q, $C_{4''}$-OCH_3), 102.2 (t, OCH_2O), 104.6 (d, $C_{2''}$ and $C_{6''}$), 108.1 (d, $C_{2'}$ or $C_{5'}$), 108.3 (d, $C_{5'}$ or $C_{2'}$), 116.2 (s, CN), 124.1 (s, $C_{4''}$), 125.4 (d, $C_{6'}$), 127.9 (s, $C_{1'}$), 131.6 (s, $C_{1''}$), 132.5 (d, C_3), 141.2 (s, C_2), 148.7 (s, $C_{3'}$ or $C_{4'}$), 152.8 (s, $C_{4'}$ or $C_{3'}$), 153.7 (s, $C_{3''}$ and $C_{5''}$), 184.9 (s, CO). EIMS *m/z*: 367 (M^+, 76.6%), 336 (M^+-OMe, 100%). X-ray powder diffraction: 11.5 (d=7.70 Å), 12.3 (d=7.20 Å), 14.4 (d=6.15 Å), 14.9 (d=5.95 Å), 16.4 (d=5.41 Å), 17.3 (d=5.13 Å), 20.0 (d=4.44 Å), 20.7 (d=4.29 Å), 21.2 (d=4.19 Å), 22.4 (d=3.97 Å), 23.1 (d=3.85 Å), 24.1 (d=3.69 Å), 24.6 (d=3.62 Å), 25.6 (d=3.48 Å), 26.1 (d=3.41 Å), 26.8 (d=3.32 Å), 28.3 (d=3.15 Å), 28.7 (d=3.11 Å), 29.0 (d=3.18 Å). **5Z-b**: Recrystallization from benzene or ethanol gave yellow fine needles, mp 168-169.5 °C. *Anal.* Calcd for $C_{20}H_{17}NO_6$: C, 65.39; H, 4.66; N, 3.81. Found: C, 65.73; H, 4.66; N, 3.56. IR cm^{-1} (KBr): 2220, 1660; ($CHCl_3$): 1660. X-ray powder diffraction: 6.5 (d=13.60 Å), 10.8 (d=8.19 Å), 11.3 (d=7.83 Å), 11.9 (d=7.44 Å), 12.8 (d=6.92 Å), 13.2 (d=6.71 Å), 14.7 (d=6.02 Å), 16.5 (d=5.37 Å), 19.0 (d=4.67 Å), 20.9 (d=4.25 Å), 22.8 (d=3.90 Å), 23.5 (d=3.79 Å), 25.4 (d=3.51 Å), 26.8 (d=3.32 Å), 28.7 (d=3.12 Å).

3-Dehydro-5-hydroxy-3-(3,4,5-trimethoxyphenyl)-5-(3,4-methylenedioxyphenyl)-2-pyrrolidone (6) To a stirred suspension of **5Z** (501 mg, 1.36 mmol) in AcOH (10 ml) was slowly added conc. H_2SO_4 (1 ml). The reaction mixture was left to stand at room temperature for 10 min in the dark, poured onto ice-water, stirred until the resulting black prepicitates turned to gray and extracted with AcOEt. The organic layer was washed with 5% NH_4OH and brine, dried over $MgSO_4$ and evaporated. Recrystallization of the residue from CH_2Cl_2-hexane gave colorless fine needles (444 mg, 84.4%), mp 166-168.5 °C (dec.). *Anal.* Calcd for $C_{20}H_{19}NO_7$: C, 62.33; H, 4.97; N, 3.64. Found: C, 62.31; H, 5.05; N, 3.66. IR cm^{-1}: 3310, 3220, 1700. UV: see Fig. 6. ^{1}H-NMR (500 MHz) δ: 3.10 (1H, s, OH), 3.86 (3H, s, $C_{4''}$-OCH_3), 3.87 (6H, s, $C_{3''}$- and $C_{5''}$-OCH_3), 5.98 (2H, s, OCH_2O), 6.43 (1H, s, NH), 6.80 (1H, d, *J*=8.3 Hz, $C_{5'}$-H), 6.98 (1H, s, C_4-H), 7.05 (1H, d, *J*=1.9 Hz, $C_{2'}$-H), 7.07 (1H, dd, *J*=8.3, 1.9 Hz, $C_{6'}$-H), 7.12 (2H, s, $C_{2''}$- and $C_{6''}$-H). ^{13}C-NMR (125 MHz) δ: 56.2 (q, $C_{3''}$- and $C_{5''}$-OCH_3), 60.9 (q, $C_{4''}$-OCH_3), 86.5 (s, C_5), 101.4 (t, OCH_2O), 104.8 (d, $C_{2''}$ and $C_{5''}$), 106.4 (d, $C_{2'}$ or $C_{5'}$), 108.3 (d, $C_{5'}$ or $C_{2'}$), 119.1 (d, $C_{6'}$), 125.6 (s, $C_{4''}$), 132.3 (s, $C_{1''}$), 132.6 (s, $C_{1'}$), 139.1 (s, C_3), 143.7 (d, C_4), 148.10 (s, $C_{3'}$ or $C_{4'}$), 148.12 (s, $C_{4'}$ or $C_{3'}$), 153.2 (s, $C_{3''}$ and $C_{5''}$), 171.5 (s, CO). EIMS *m/z*: 367 (M^+-H_2O, 100%).

3-Dehydro-5-methoxy-3-(3,4,5-trimethoxyphenyl)-5-(3,4-methylenedioxyphenyl)-2-pyrrolidone (7) A solution of **6** (200 mg, 0.519 mmol) in MeOH (10 ml) containing a catalytic amount of *p*-TsOH was refluxed for 10 min. The reaction mixture was extracted with AcOEt. The organic layer was dried over $MgSO_4$ and evaporated. The residue was recrystallized from MeOH to afford colorless fine needles (152 mg, 73.4%), mp 154-160 °C (dec.). *Anal.* Calcd for $C_{21}H_{21}NO_7$ 2/5MeOH:

C, 62.35; H, 5.53; N, 3.40. Found: C, 62.19; H, 5.42; N, 3.40. IR cm^{-1}: 3325, 1710. UV nm (log ε) (dioxane): 237 (4.24)sh, 298 (4.06), 311 (4.07)sh. ^{1}H-NMR (500 MHz) δ: 3.37 (3H, s, C_5-OCH_3), 3.87 (3H, s, $C_{4''}$-OCH_3), 3.89 (6H, s, $C_{3''}$- and $C_{5''}$-OCH_3), 5.97 (2H, s, OCH_2O), 6.22 (1H, s, NH), 6.79 (1H, d, *J*=7.8 Hz, $C_{5'}$-H), 6.88 (1H, s, C_4-H), 7.04 (1H, d, *J*=1.7 Hz, $C_{2'}$-H), 7.05 (1H, dd, *J*=7.8, 1.7 Hz, $C_{6'}$-H), 7.17 (2H, s, $C_{2''}$- and $C_{6''}$-H). ^{13}C-NMR (125 MHz) δ: 50.8 (q, C_5-OCH_3), 56.2 (q, $C_{3''}$- and $C_{5''}$-OCH_3), 60.9 (q, $C_{4''}$-OCH_3), 90.5 (s, C_5), 101.4 (t, OCH_2O), 104.9 (d, $C_{2''}$ and $C_{5''}$), 106.6 (d, $C_{2'}$ or $C_{5'}$), 108.3 (d, $C_{5'}$ or $C_{2'}$), 119.2 (d, $C_{6'}$), 125.6 (s, $C_{4''}$), 132.3 (s, $C_{1''}$), 134.7 (s, $C_{1'}$), 139.3 (s, C_3), 142.1 (d, C_4), 148.05 (s, $C_{3'}$ or $C_{4'}$), 148.13 (s, $C_{4'}$ or $C_{3'}$), 153.3 (s, $C_{3''}$ and $C_{5''}$), 171.5 (s, CO). EIMS *m/z*: 399 (M^+, 1.7%), 367 (M^+-MeOH, 100%).

(Z)-2-(3,4,5-Trimethoxyphenyl)-4-(3,4-methylenedioxyphenyl)-4-oxo-2-butenoic Acid (8Z)

a) From the (Z)-Nitrile (5Z) A solution of **5Z** (10.0 g, 27.2 mmol) in MeOH (60 ml) and 10% NaOH (60 ml) was refluxed for 1.5 h in the dark. After cooling, the mixture was diluted with water, acidified with 10% HCl and then extracted with CH_2Cl_2. The organic solution was dried over Na_2SO_4 and evaporated. Recrystallization of residue from EtOH afforded yellow needles (9.03 g, 85.8%), mp 152-156 °C (dec.). *Anal.* Calcd for $C_{20}H_{18}O_8$ 1/4H_2O: C, 61.46; H, 4.77. Found: C, 61.30; H, 4.74. IR cm^{-1}: 3225, 1730, 1640; ($CHCl_3$): 1770. UV: see Fig. 6. ^{1}H-NMR (acetone-d_6) δ: 3.75 (3H, s, $C_{4''}$-OCH_3), 3.85 (6H, s, $C_{3''}$- and $C_{5''}$-OCH_3), 6.01 (2H, s, OCH_2O), 6.85 (1H, d, J=8.5 Hz, $C_{5'}$-H), 7.00-7.40 (7H, m, Ar-H, OH and/or olefinic H), 7.71 (1H, s, Ar-H or olefinic H). EIMS *m/z*: 386 (M^+, 52.5%), 28 (100%).

b) From the Hydroxypyrrolidone (6) Reacting a solution of **6** (100 mg, 0.259 mmol) in MeOH (4 ml) and 10% NaOH (4 ml) for 30 min as above gave **8Z** (89 mg, 86.7%).

c) From the (*E*)-Nitrile (5E) Reacting a solution of **5E** (100 mg, 0.272 mmol) in MeOH (4 ml) and 10% NaOH (4 ml) for 1h as above gave **8Z** (84 mg, 80.0%).

Photoisomerization of the (Z)-Acid (8Z) [(*E*)-2-(3,4,5-Trimethoxyphenyl)-4-(3,4-methylenedioxyphenyl)-4-oxo-2-butenoic Acid (8E-a)] A solution of **8Z** (502 mg, 1.29 mmol) in acetone (500 ml) was irradiated with Daylight lamp® at room temperature for 48 h and then the reaction mixture was evaporated. The residue was purified by fractional recrystallization from $CHCl_3$-hexane to afford pale yellow fine needles (422 mg, 84.1%), mp 194-198 °C (dec.). *Anal.*Calcd for $C_{20}H_{18}O_8$: C, 62.17; H, 4.70. Found: C, 62.27; H, 4.66. IR cm^{-1}: 1700, 1660. UV nm (log ε) (MeOH): 234 (4.27)sh, 277 (3.91)sh, 322 (3.97); (AcOEt): 273 (3.91), 318 (3.97). ^{1}H-NMR (400 MHz) δ: 3.73 (6H, s, $C_{3''}$- and $C_{5''}$-OCH_3), 3.78 (3H, s, $C_{4''}$-OCH_3), 3.8-5.5 (1H, dif. s, COOH), 6.02 (2H, s, OCH_2O), 6.48 (2H, s, $C_{2''}$- and $C_{6''}$-H), 6.75 (1H, d, *J*=8.1 Hz, $C_{5'}$-H), 7.29 (1H, d, *J*=1.7 Hz, $C_{2'}$-H), 7.42 (1H, dd, *J*=8.1, 1.7 Hz, $C_{6'}$-H), 7.66 (1H, s, C_3-H). EIMS *m/z*: 386 (M^+, 21.0%), 149 (25.9%), 28 (100%). **8E-b**: Thermal transition at 130 °C for 72 h under reduced pressure gave yellow fine needles, mp 198-200 °C (dec.). *Anal.* Calcd $C_{20}H_{18}O_8$: C, 62.17; H, 4.70. Found: C, 62.27; H, 4.65. IR cm^{-1}: 1700, 1635, 1615. **8E-c**: Recrystallization from CH_2Cl_2-Et_2O gave colorless fine needles, mp 194-198 °C (dec.). *Anal.* Calcd for $C_{20}H_{18}O_8$: C, 62.17; H, 4.70. Found: C, 62.01; H, 4.49. IR cm^{-1}: 1720, 1660. **8E-d**: Recrystallization from benzene-CH_2Cl_2-hexane gave pale yellow needles, mp 199-202 °C (dec.). *Anal.* Calcd for $C_{20}H_{18}O_8$: C, 62.17; H, 4.70. Found: C, 62.12; H, 4.46. IR cm^{-1}: 1715sh, 1705, 1665, 1640, 1620.

Methylation of the Acid (8) [Methyl 2-(3,4,5-Trimethoxyphenyl)-4-(3,4-methylenedioxyphenyl)-4-oxo-2-butenoate (9)] A mixture of **8**, K_2CO_3 and Me_2SO_4 in acetone was stirred at room temperature, poured onto ice-water and 10% NH_4OH and then extracted with CH_2Cl_2. The organic layer was washed with 5% $NaHCO_3$, dried over Na_2SO_4 and evaporated.

a) On the (Z)-Acid (8Z) A mixture of **8Z** (10.0 g, 25.9 mmol), K_2CO_3 (7.15 g, 51.8 mmol) and Me_2SO_4 (4.9 ml, 51.8 mmol) in acetone (200 ml) was reacted for 3 h. Recrystallization of the crude product from CH_2Cl_2-Et_2O afforded **9Z** (8.753 g, 84.5%) as yellow needles, mp 156.5-157.5 °C. *Anal.* Calcd for $C_{21}H_{20}O_8$: C, 62.99; H, 5.04. Found: C, 63.09; H, 5.07. IR cm^{-1}: 1740, 1725, 1650. UV nm (log ε) (EtOH): 242 (4.15), 351 (4.29). ^{1}H-NMR (270 MHz) δ: 3.89 (3H, s, OCH_3), 3.90 (6H, s, OCH_3), 3.93 (3H, s, OCH_3), 6.07 (2H, s, OCH_2O), 6.78 (2H, s, C_2''- and C_6''-H), 6.89 (1H, d, J=8.2 Hz, C_5'-H), 7.19 (1H, s, C_3-H), 7.49 (1H, d, J=1.5 Hz, C_2'-H), 7.61 (1H, dd, J=8.2, 1.5 Hz, C_6'-H). ^{13}C-NMR (67.5 MHz) δ: 52.7 (q, COO$\underline{C}H_3$), 56.3 (q, C_3''- and C_5''-OCH_3), 61.0 (q, C_4''-OCH_3), 102.0 (t, OCH_2O), 104.7 (d, C_2'' and C_6''), 108.0 (d, C_2' or C_5'), 108.3 (d, C_5' or C_2'), 122.2 (d, C_6'), 125.1 (d, C_3), 129.7 (s, C_2), 132.2 (s, C_4''), 140.5 (s, C_1'), 147.2 (s, C_1''), 148.5 (s, C_3' or C_4'), 152.2 (s, C_4' or C_3'), 153.5 (s, C_3'' and C_5''), 169.1 (s, $\underline{C}OOCH_3$), 186.8 (s, CO). EIMS *m/z*: 400 (M$^+$, 92.0%), 369 (M$^+$-OMe, 100%). **The Crystal Data**^{15}: See Table 2. The reflection data were collected for $3° < 2θ < 155°$using CuK$_α$ radiation (λ=1.54178 Å) and the $ω < 30° < ω$-$2θ$ scan method at a 2θ scan speed 4°/min. A total of 7857 independent reflections were collected, of which $5755/3° < 2θ < 120°$ reflections with $F_o > 3σ(F_o)$ were used for calculation. The final *R* value was 0.0582.

b) On the (*E*)-Acid (8E) A mixture of **8E** (203 mg, 0.53 mmol), K_2CO_3 (144 mg, 1.04 mmol) and Me_2SO_4 (0.1 ml, 1.06 mmol) in acetone (8 ml) was reacted for 1h. Recrystallization of the crude product from Et_2O-hexane afforded **9E** (202 mg, 96.2%) as colorless needles, mp 108-110 °C. *Anal.* Calcd for $C_{21}H_{20}O_8$: C, 62.99; H, 5.04. Found: C, 63.22; H, 5.06. IR cm^{-1}: 1720, 1660. UV nm (log ε) (EtOH): 232 (4.29), 274 (3.89), 323 (3.97). ^{1}H-NMR (270 MHz) δ: 3.72 (6H, s, OCH_3), 3.78 (3H, s, OCH_3), 3.88 (3H, s, OCH_3), 6.01 (2H, s, OCH_2O), 6.45 (2H, s, C_2''- and C_6''-H), 6.74 (1H, d, J=8.0 Hz, C_5'-H), 7.28 (1H, d, J=1.5 Hz, C_2'-H), 7.41 (1H, dd, J=8.0, 1.5 Hz, C_6'-H), 7.51 (1H, s, C_3-H). EIMS *m/z*: 400 (M$^+$, 67%), 369 (M$^+$-OMe, 100%). **The Crystal Data**^{15}: See Table 2. The reflection data were collected for $3° < 2θ < 140°$using CuK$_α$ radiation (λ=1.54178 Å) and the $ω < 30° < ω$-$2θ$ scan method at a 2θ scan speed 4°/min. A total of 4252 independent reflections were collected, of which $2841/3° < 2θ < 120°$ reflections with $F_o > 3σ(F_o)$ were used for calculation. The final *R* value was 0.0604.

Solid State Photoreaction of the Nitrile (5)

a) On the (Z)-Nitrile (5Z) [1,*t*-2-bis(3,4,5-Trimethoxyphenyl)-*c*-3,*c*-4-bis(3,4-methylenedioxybenzoyl)-*r*-1,*c*-2-cyclobutanedinitrile (10)] **5Z-b** (0.275 g, 0.749 mmol) was exposed to sunlight for 4 h. The reaction mixture was dissolved in minimum amount of CH_2Cl_2 and added to AcOEt. The resulting prepicitates were collected by filtration and washed with AcOEt. Recrystallization of the prepicitates from CH_2Cl_2-hexane gave colorless fine prisms (0.193 g, 70.2%), mp 141-144 °C (dec.). *Anal.* Calcd for $C_{40}H_{34}N_2O_{12}$: C, 65.39; H, 4.66; N, 3.81. Found: C, 65.20;

H, 4.66; N, 3.61. IR cm^{-1}: 1675. UV nm (log ε) (dioxane): 226 (4.69)sh, 278 (4.20), 314 (4.22). ^{1}H-NMR (500 MHz) δ: 3.73 (12H, s, $C_{3'}$-, $C_{5'}$-, $C_{3''}$- and $C_{5''}$-OCH_3), 3.78 (6H, s, $C_{4'}$- and $C_{4''}$-OCH_3), 4.88 (2H, s, C_3- and C_4-H), 6.04 (4H, s, OCH_2O), 6.45 (4H, s, $C_{2'}$, $C_{6'}$-, $C_{2''}$- and $C_{6''}$-H), 6.80 (2H, d, *J*=8.0 Hz, $C_{5'''}$- and $C_{5''''}$-H), 7.31 (2H, dd, *J*=8.0, 1.7 Hz, $C_{6'''}$- and $C_{6''''}$-H), 7.38 (2H, d, *J*=1.7 Hz, $C_{2'''}$- and $C_{2''''}$-H). ^{13}C-NMR (125 MHz, DMSO-*d*$_6$) δ: 46.9 (d, C_3 and C_4), 52.6 (s, C_1 and C_2), 56.1 (q, $C_{3'}$-, $C_{5'}$-, $C_{3''}$- and $C_{5''}$-OCH_3), 59.8 (q, $C_{4'}$- and $C_{4''}$-OCH_3), 102.1 (t, OCH_2O), 105.5 (d, $C_{2'}$, $C_{2''}$, $C_{6'}$ and $C_{6''}$), 107.6 (d, $C_{2'''}$ and $C_{2''''}$ or $C_{5'''}$ and $C_{5''''}$), 108.1 (d, $C_{5'''}$ and $C_{5''''}$ or $C_{2'''}$ and $C_{2''''}$), 118.3 (s, C_1- and C_2-CN), 125.0 (d, $C_{6'''}$ and $C_{6''''}$), 126.8 (s, $C_{4'}$ and $C_{4''}$), 129.5 (s, $C_{1'}$ and $C_{1''}$), 138.1 (s, $C_{1'''}$ and $C_{1''''}$), 147.8 (s, $C_{3'''}$ and $C_{3''''}$ or $C_{4'''}$ and $C_{4''''}$), 151.8 (s, $C_{4'''}$ and $C_{4''''}$ or $C_{3'''}$ and $C_{3''''}$), 152.6 (s, $C_{3'}$, $C_{3''}$, $C_{5'}$ and $C_{5''}$), 192.1 (s, CO). EIMS *m/z*: 367 (monomer, 100 %). FABMS *m/z*: 735 (M^++1). **The Crystal Data**[15]: Molecular formula, $C_{40}H_{34}N_2O_{12}$ C_3H_6O[16]; molecular weight, 792.77; crystal system, monoclinic; space group, $P2_1/n$ with unit cell dimensions a=19.076(11) Å, b=15.176(22) Å, c=13.999(7) Å, β=102.64(4) Å, U=3954.73 Å^3, Z=4, D=1.332 gcm^{-3}. The reflection data were collected for 3°<2θ<120°using CuK_α radiation (λ=1.54178 Å) and the ω<30°<ω-2θ scan method at a 2θ scan speed 4°/min. A total of 5131 independent reflections were collected, of which 4279 reflections with $F_o>3\sigma(F_o)$ were used for calculation. The final *R* value was 0.0606.

b) On the (*E*)-Nitrile (5E) 5E (1.003 g, 2.73 mmol) was exposed to sunlight for 37.5 h. The reaction mixture was purified by column chromatography with hexane-acetone (2 : 1, v/v) followed by benzene-AcOEt (10 : 1, v/v). The starting **5E** (0.338 g, 33.7%), the isomerized **5Z** (0.278 g, 27.7%) and the (Z-Z)-dimer (**10**) (0.110 g, 11.0%) were given from the first, the second and the last eluates, respectively.

1,*t*-2-bis(3,4,5-Trimethoxyphenyl)-*c*-3,*t*-4-bis(3,4-methylenedioxybenzoyl)-*r*-1,*c*-2-cyclobutanedinitrile (11) The third fraction afforded colorless fine needles (0.147 g, 14.6%), mp 117-120 °C (dec.), which were recrystallized from CH_2Cl_2-hexane to give colorless fine prisms, mp 134-136 °C (dec.). *Anal.* Calcd for $C_{40}H_{34}N_2O_{12}$: C, 65.39; H, 4.66; N, 3.81. Found: C, 65.29; H, 4.60; N, 3.51. IR cm^{-1}: 1660. UV nm (log ε) (dioxane): 233 (4.67), 280 (4.25), 320 (4.31). ^{1}H-NMR (500 MHz) δ: 3.59 (6H, s, $C_{3'}$- and $C_{5'}$-OCH_3), 3.69 (3H, s, $C_{4'}$- or $C_{4''}$-OCH_3), 3.71 (6H, s, $C_{3''}$- and $C_{5''}$-OCH_3), 3.76 (3H, s, $C_{4'}$- or $C_{4''}$-OCH_3), 5.34 (1H, d, *J*=10.4 Hz, C_3-H), 5.44 (1H, d, *J*=10.4 Hz, C_4-H), 6.03 (2H, s, OCH_2O), 6.05 (1H, d, *J*=1.1 Hz, $OC\underline{H}HO$), 6.06 (1H, d, *J*=1.1 Hz, $OCH\underline{H}O$), 6.30 (2H, s, $C_{2'}$- and $C_{6'}$-H), 6.43 (2H, s, $C_{2''}$- and $C_{6''}$-H), 6.73 (1H, d, *J*=8.0 Hz, $C_{5'''}$-H), 6.91 (1H, d, *J*=8.0 Hz, $C_{5''''}$-H), 7.45 (1H, d, *J*=1.7 Hz, $C_{2''''}$-H), 7.47 (1H, d, *J*=1.7 Hz, $C_{2'''}$-H), 7.50 (1H, dd, *J*=8.0, 1.7 Hz, $C_{6''''}$-H), 7.79 (1H, dd, *J*=8.0, 1.7 Hz, $C_{6'''}$-H). ^{13}C-NMR (100 MHz, DMSO-*d*$_6$) δ: 45.6 (d, C_3 or C_4), 47.0 (d, C_4 or C_3), 54.0 (s, C_1 or C_2), 54.3 (s, C_2 or C_1), 55.6 (q, $C_{3'}$- and $C_{5'}$-OCH_3 or $C_{3''}$- and $C_{5''}$-OCH_3), 56.1 (q, $C_{3''}$-and $C_{5''}$-OCH_3 or $C_{3'}$- and $C_{5'}$-OCH_3), 59.7 (q, $C_{4'}$- or $C_{4''}$-OCH_3), 59.8 (q, $C_{4''}$- or $C_{4'}$-OCH_3), 102.3 (t, OCH_2O), 102.4 (t, OCH_2O), 105.4 (d, $C_{2'}$ and $C_{6'}$ or $C_{2''}$ and $C_{6''}$), 105.6 (d, $C_{2''}$ and $C_{6''}$ or $C_{2'}$ and $C_{6'}$), 107.2, 108.1, 108.4 (each d, $C_{2'''}$, $C_{2''''}$, $C_{5'''}$, $C_{5''''}$), 118.3 (s, C_1- or C_2-CN), 119.5 (s, C_2- or C_1-CN), 124.4 (s, $C_{4'}$ or $C_{4''}$), 125.0 (s, $C_{6'''}$ or $C_{6''''}$), 125.4 (s, $C_{4''}$ or $C_{4'}$), 125.9 (s, $C_{6''''}$ or $C_{6'''}$), 128.5 (s, $C_{1'}$ or $C_{1''}$), 129.6 (s, $C_{1''}$ or $C_{1'}$), 137.8 (s, $C_{1'''}$ or $C_{1''''}$), 138.2 (s, $C_{1''''}$ or $C_{1'''}$), 147.9 and 148.2 (each s, $C_{3'''}$ and $C_{4'''}$), 152.3 and 152.46 (each s, $C_{3'''}$ and $C_{4'''}$), 152.52 and 152.7 (each s, C3' and C5'), 192.9 and 194.2 (each s, CO). EIMS *m/z*: 734 (M^+, 3.8%), 367 (monomer, 40%), 149 (100%). HRMS *m/z*: 734.2110 (Calcd for $C_{40}H_{34}N_2O_{12}$: 734.2109). **The Crystal Data**[15]: Molecular formula, $C_{40}H_{34}N_2O_{12}$ $2(C_3H_6O)$[16]; molecular weight, 850.84; crystal system, triclinic; space group, $P\bar{1}$ with unit cell dimensions a=12.155(7) Å, b=16.978(14) Å, c=11.612(16) Å, α=107.95(9)°, β=105.25(9)°, γ=78.77(6)°, U=2182.78 Å^3, Z=2, D=1.118 gcm^{-3}. The reflection data were collected for $3° < 2\theta < 120°$ using CuK_α radiation (λ=1.54178 Å) and the $\omega < 30° < \omega\text{-}2\theta$ scan method at a 2θ scan speed 4°/min. A total of 4884 independent reflections were collected, of which 3928 reflections with $F_o > 3\sigma(F_o)$ were used for calculation. The final *R* value was 0.1622.[17]

Epimerization of the (*Z*-*Z*)-Dimer (10) [The (*E*-*Z*)-Dimer (11)] A solution of **10** (53 mg, 72.4 μmol) in CH_2Cl_2 (5 ml) containing SiO_2 (0.881 g) was stirred at room temperature for 18 h. After removal of the SiO_2 by filtration, the filtrate was evaporated. Recrystallization of the residue from CH_2Cl_2-hexane afforded **11** (46 mg, 86.8%).

Photoreaction of the (Z)-Nitrile (5Z) in Solution [The (*E*)-Nitrile (5E)] A solution of **5Z** (99.8 mg, 0.272 mmol) in AcOEt (200 ml) was placed into a PYREX® flask and irradiated with Daylight lamp® for 24 h. After evaporation recrystallization of the residue from benzene-hexane afforded **5E** (81.1 mg, 81.4%).

Thermal Isomerization of the (*E*)-Nitrile (5E) A solution of **5E** in either MeOH or CD_3OD was refluxed in the dark. After cooling, the resulting precipitates was collected by filtration and washed with MeOH or benzene.

a) In MeOH Refluxing **5E** (500 mg, 1.36 mmol) in MeOH (50 ml) for 8 h followed by washings with MeOH afforded **5Z** (401 mg, 80.0%).

b) In CD_3OD [(*Z*)-2-(3,4,5-Trimethoxyphenyl)-3-(3,4-methylenedioxybenzoyl)-[3-^{2}H]acrylonitrile] Refluxing **5E** (51 mg, 0.139 mmol) in CD_3OD (1 ml) for 10 min followed by washings with benzene afforded yellow fine needles (33 mg, 64.5%), mp 168-169.5 °C. IR cm^{-1}: 1660. ^{1}H-NMR (400 MHz) δ: 3.92 (3H, s, C4''-OCH_3), 3.95 (6H, s, C3''- and C5''-OCH_3), 6.10 (2H, s, OCH_2O), 6.91 (1H, d, *J*=8.2 Hz, C5'-H), 6.99 (2H, s, C2''- and C6''-H), 7.53 (1H, d, *J*=1.7 Hz, C2'-H), 7.61 (1H, dd, *J*=8.2, 1.7 Hz, C6'-H). EIMS *m/z*: 369 (M^++1, 22.3%), 368 (M^+, 100%), 337 (M^+-OMe, 95.3%).

Solid State Photoreaction of the (Z)-Ester (9Z) **9Z** (103 mg, 0.258 mmol) was irradiated with Daylight lamp® for 36 h. The reaction mixture was purified by column chromatography with AcOEt-benzene (1 : 7, v/v) followed by AcOEt. The starting **9Z** (14.3 mg, 13.8%) and the isomerized **9E** (16.6 mg, 16.1%) were given from the first and second fractions, respectively.

Dimethyl 1,*t*-3-bis(3,4,5-Trimethoxyphenyl)-*c*-2,*t*-4-bis(3,4-methylenedioxybenzoyl)-*r*-1,*t*-3-cyclobutanedicarboxylate (13) The third fraction gave colorless fine needles (54.4 mg, 52.7%), mp 278-280 °C (dec.), which were recrystallized from CH_2Cl_2-Et_2O. *Anal.* Calcd $C_{42}H_{40}O_{16}$: C, 62.99; H, 5.04. Found: C, 62.82; H, 5.10. IR cm^{-1}: 1730, 1670. UV nm (log ε) (EtOH): 236 (4.61), 281 (4.11), 322 (4.28). ^{1}H-NMR (400 MHz) δ: 3.52 (6H, s,

$C_{4'}$- and $C_{4'''}$-OCH_3), 3.58 (12H, s, $C_{3'}$-, $C_{5'}$-, $C_{3'''}$- and $C_{5'''}$-OCH_3), 3.78 (6H, s, $COOCH_3 \times 2$), 6.07 (4H, s, $OCH_2O \times 2$), 6.33 (6H, s, C_2-, C_4-H, $C_{2'}$-, $C_{6'}$-, $C_{2'''}$- and $C_{6'''}$-H), 6.96 (2H, d, *J*=8.2 Hz, $C_{5''}$- and $C_{5''''}$-H), 7.51 (2H, d, *J*=1.8 Hz, $C_{2''}$- and $C_{2''''}$-H), 8.04 (2H, dd, *J*=8.2, 1.8 Hz, $C_{6''}$- and $C_{6''''}$-H). ^{13}C-NMR (100 MHz) δ: 51.1 (d, C_2 and C_4), 52.6 (q, $COO\underline{C}H_3 \times 2$), 54.1 (s, C_1 and C_3), 55.7 (q, $C_{2'}$-, $C_{6'}$-, $C_{2'''}$- and $C_{6'''}$-OCH_3), 60.8 (q, $C_{4'}$- and $C_{4'''}$-OCH_3), 102.1 (t, $OCH_2O \times 2$), 104.6 (d, $C_{2'}$, $C_{6'}$, $C_{2'''}$ and $C_{6'''}$), 108.2 (d, $C_{2''}$ and $C_{2''''}$ or $C_{5''}$ and $C_{5''''}$), 125.2 (d, $C_{6''}$ and $C_{6''''}$), 132.9 (s, $C_{4'}$ and $C_{4''''}$), 133.3 (s, $C_{1''}$and $C_{1''''}$), 137.1 (s, $C_{1'}$ and $C_{1''''}$), 148.6 (s, $C_{3''}$ and $C_{3''''}$ or $C_{4''}$ and $C_{4''''}$), 152.3 (s, $C_{4''}$ and $C_{4''''}$ or $C_{3''}$ and $C_{3''''}$), 152.8 (s, $C_{3'}$, $C_{5'}$, $C_{3'''}$ and $C_{5'''}$), 174.3 (s, $\underline{C}OOCH_3 \times 2$), 194.4 (s, $CO \times 2$). EIMS *m/z*: 800 (M^+, 50%), 400 (monomer, 55%), 149(100%). HRMS *m/z*: 800.2294 (Calcd for $C_{42}H_{40}O_{16}$: 800.2313). **The Crystal Data**[15]: Molecular formula, $C_{42}H_{40}O_{16}$; molecular weight, 800.00; crystal system, triclinic; space group, $P\bar{1}$ with unit cell dimensions a=10.742(4) Å, b=14.279(6) Å, c=8.014(4) Å, α=108.55(4)°, β=108.70(4)°, γ=73.44(3)°, U=1080.63 $Å^3$, Z=1 (1/2 mol in an asymmetric unit), D=1.230 gcm^{-3}. The reflection data were collected for $3° < 2\theta < 140°$using CuK_α radiation (λ=1.54178 Å) and the $\omega < 30° < \omega-2\theta$ scan method at a 2θ scan speed 4°/min. A total of 3349 independent reflections were collected, of which 2824/$3° < 2\theta < 120°$ reflections with $F_o > 3\sigma(F_o)$ were used for calculation. The final *R* value was 0.0757.[18]

Solid State Photoreaction of the (Z)-Acid (8Z) **8Z** (308 mg, 0.797 mmol) was irradiated with Daylight lamp® for 62 h. The reaction mixture was suspended in CH_2Cl_2 containing a minimum amount of acetone and filtered. From the filtrate the starting **8Z** (103 mg, 33.4%) and the isomerized **8E** (76 mg, 24.6%) were obtained.

1,*t*-3-bis(3,4,5-Trimethoxyphenyl)-*c*-2,*t*-4-bis(3,4-methylenedioxybenzoyl)-*r*-1,*t*-3-cyclobutanedicarboxylic Acid (14) Recrystallization of the solid from dioxane gave colorless prisms (54 mg, 17.5%), mp 292-296 °C (dec.). *Anal.* Calcd for $C_{40}H_{36}O_{16}$: C, 62.17; H, 4.70. Found: C, 61.84; H, 4.76. IR cm^{-1}: 1700, 1665. ^1H-NMR (500 MHz, DMSO-d_6) δ: 3.48 (12H, s, $C_{3'}$-, $C_{5'}$-, $C_{3'''}$- and $C_{5'''}$-OCH_3), 3.60 (6H, s, $C_{4'}$- and $C_{4'''}$-OCH_3), 6.12 (2H, s, C_2- and C_4-H), 6.18 (4H, s, $OCH_2O \times 2$), 6.33 (4H, s, $C_{2'}$-, $C_{6'}$-, $C_{2'''}$- and $C_{6'''}$-H), 7.21 (2H, d, *J*=8.0 Hz, $C_{5''}$- and $C_{5''''}$-H), 7.40 (2H, d, *J*=1.7 Hz, $C_{2''}$- and $C_{2''''}$-H), 7.94 (2H, dd, *J*=8.0, 1.7 Hz, $C_{6''}$- and $C_{6''''}$-H), 12.57 (2H, s, $COOH \times 2$). FABMS *m/z*: 818 (M^++2Na), 773 (M^++1).

Methylation of the Dimer (14) [The Ester Dimer (13)] A solution of **14** (51 mg, 0.066 mmol) in dioxane (25 ml) was treated with large excess of diazomethane at room temperature for 12 h. After addition of AcOH (2 drops), the resulting solution was evaporated. The residue was recrystallized from CH_2Cl_2-Et_2O to afford **13** (47 mg, 88.9%).

HPLC Analysis for the Photoreactions For **5** and **9** were used benzene-AcOEt (1 : 1 and 1 : 6, v/v) and for **8** hexane-AcOEt-AcOH (20 : 20 : 1, v/v/v) as mobile phases, respectively. The flow rate was 1 ml/min and each peak was detected with UV (310 nm for **5**, 330 nm for **8** and 320 nm for **9**).

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