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Solid-State Photodimerization of Methyl (*RS*)-1-Phenyl-2-piperidinoethyl (*RS*)-1,4-Dihydro-2,6-dimethyl-4-(2-thiazolyl)pyridine-3,5-dicarboxylate Hydrochloride Controlled by the Buffer Zone

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The solid-state photodimerization of three polymorphic crystal forms (forms I, II, and III) of a bulky olefin, methyl (*RS*)-1-phenyl-2-piperidinoethyl (*RS*)-1,4-dihydro-2,6-dimethyl-4-(2-thiazolyl)pyridine-3,5-dicarboxylate hydrochloride, was studied. Forms I and II are anhydrous crystals and form III is an isomorphous hydrate of form II. X-Ray analyses of these forms showed that forms II and III have the same geometrical characteristics suggesting high susceptibility to photodimerization according to the well-known topochemical rule. Although UV irradiation of from II affords a photodimer, 4a,8a-dimethoxycarbonyl-2,4b,6,8b-tetramethyl-3-[(*RS*)-1-phenyl-2-piperidinoethoxycarbonyl]-7-[(*SR*)-1-phenyl-2-piperidinoethoxycarbonyl]-(4*RS*,8*SR*)-4,8-di(2-thiazolyl)-1,4,4a,4b,5,8,8a,8b-octahydro-*cis-transoid*-4a,4b-*cis*-cyclobuta[1,2-*b* : 3,4-*b*′]dipyridine, in high yield, the photolysis of form III proceeds much more slowly than that of form II. A detailed inspection of the crystal structures revealed that there is a space to afford the mobility of molecules for dimerization in form II, whereas the space is occupied by the incorporated water molecule in form III. We have previously proposed that a buffer zone, which is a space in the crystal structure, controls the photodimerization of bulky olefins. The present study demonstrates that the buffer zone is an essential controlling factor for the solid-state photodimerization of bulky olefins.

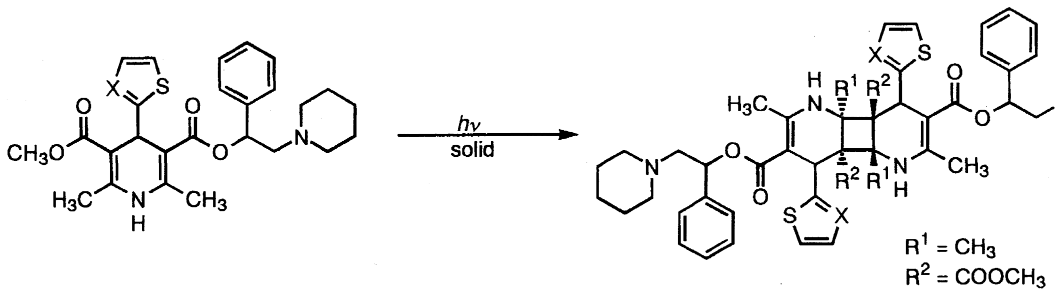
The solid-state photodimerization of olefins is one of the well-known topochemical photoreactions.[1] A topochemical rule describing the relationships between the crystal structures of olefins and the photoreactivity was first established by Schmidt and his co-workers based on the photodimerization of cinnamic acid derivatives.[2] According to Schmidt's rule, the packing arrangement of the monomer crystal determines the reactivity, i.e. the reacting double bonds should be in parallel with the center-to-center distance of 4.2 Å, or less, for photodimerization. Since the pioneering work by Schmidt and his group, however, some examples in which a reaction does not occur in spite of the favorable crystal packing for photodimerization have been reported.[1,3] These exceptions have been explained in terms of Cohen's "reaction cavity" principle, which states that solid-state reactions proceed with minimal distortion of the surface of the reaction cavity.[4] Gavezzotti also generalized that a prerequisite for crystal reactivity is the availability of free space around the reaction site.[5] On the basis of these principles, it seems that bulky olefins should not undergo solid-state photodimerization due to the significant steric hindrance, even though the arrangement of double bonds satisfies Schmidt's rule. However, no systematic studies have been made on the solid-state photodimerization of bulky olefins.

We discovered that bulky olefins can undergo solid-state photodimerization in spite of a highly steric hindrance. In a previous paper, we reported that methyl (*RS*)-1-phenyl-2-piperidinoethyl (*RS*)-1,4-dihydro-2,6-dimethyl-4-(2-thienyl)-pyridine-3,5-dicarboxylate (**1**) photodimerizes to **2** in the crystal (Scheme 1), and discussed its reactivity based on the crystal structure.[6] The photoreactivity cannot be explained by Schmidt's rule and/or the other above-mentioned principles. To explain the crystal structure-reactivity relationships, we have introduced a new concept of "buffer zone" in the crystal structure. The buffer zone is defined as a disordered packing region in the crystal to maintain the crystal structure in the monomer state and to afford the mobility of the monomer molecules for dimerization. We proposed that only a crystal which satisfies Schmidt's rule and possesses a buffer zone in the crystal structure can undergo solid-state photodimerization.

In this paper we report a second example of the buffer zone that governs the photodimerization of bulky olefins. An analog of **1**, methyl (*RS*)-1-phenyl-2-piperidinoethyl (*RS*)-1,4-dihydro-2,6-dimethyl-4-(2-thiazolyl)pyridine-3,5-dicarboxylate hydrochloride (**3**), crystallizes in three crystal forms; one of them gives a photodimer (**4**) upon UV irradiation using the buffer zone in the crystal (Scheme 1).

Results and Discussion

Photochemical Behavior of Polymorphs. In the course of developing of calcium channel antagonists, compound **3**



1: X = CH
3: X = N (HCl salt)

2: X = CH
4: X = N (HCl salt)

Scheme 1.

was synthesized.[7] Changes in the recrystallizing conditions of **3** revealed that it exists in at least two crystalline forms, designated as forms I and II. Form I, obtained from acetonitrile, is a non-hygroscopic anhydrate form, and form II, obtained from ethyl acetate–ethanol, is a hygroscopic anhydrate form. Forms I and II can be clearly differentiated by IR or X-ray powder diffraction. Form II easily uptakes water to convert to a monohydrate form (form III) upon exposure to the ambient relative humidity, and by dehydration upon heating form III reversibly changes into form II. IR and X-ray powder diffraction showed that forms II and III are isomorphous. A thermogravimetric (TG) analysis of form III demonstrated that water is lost up to 40 °C, indicating that the water molecules in form III are loosely bound in the crystal.

Photochemical studies on the three modifications demonstrated that form I is photostable, whereas forms II and III are unstable to UV irradiation.[8] Forms II and III give the same photoproducts, one major product (**4**) and two minor products.[9] However, the photodegradation rate for forms II and III are remarkably different. Form II affords **4** in 58% yield with 22% recovery of **3** on UV irradiation by a chemical lamp (320—400 nm) for 8 h whereas form III gives **4** in only 2% yield with 98% recovery of **3** under the same conditions. This obviously indicates that the existence of the incorporated water in the crystal affects their photostabilities. In order to determine the structure of photoproduct **4**, X-ray analysis was undertaken. As shown in Fig. 1, it was found that **4** is a centrosymmetric photodimer having a crystallographic center of inversion. Crystallographic data and selected geometrical parameters for **4** are listed in Tables 1 and 2, respectively, and the crystal structure of **4** is depicted in Fig. 2. The 1,4,4a,4b,5,8,8a,8b,-octahydrocyclobuta[1,2-*b* : 3,4-*b*′]dipyridine moiety adopts a *cis-transoid-cis* configuration and the tetrahydropyridine ring adopts a boat shape

Table 1. Crystallographic Data for **3** (Forms I, II, and III) and **4**

	Form I	Form II	Form III	**4**
Formula	$C_{26}H_{31}N_3O_4S{\cdot}HCl$	$C_{26}H_{31}N_3O_4S{\cdot}HCl$	$C_{26}H_{31}N_3O_4S{\cdot}HCl{\cdot}H_2O$	$C_{52}H_{62}N_6O_8S_2{\cdot}2HCl{\cdot}6H_2O$
Formula weight	518.07	518.07	536.09	1144.23
Color; habit	Colorless, prism	Colorless, plate	Colorless, plate	Colorless, plate
Size/mm	0.30 × 0.30 × 0.20	0.35 × 0.30 × 0.10	0.35 × 0.20 × 0.15	0.30 × 0.25 × 0.20
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	12.482(3)	11.575(1)	11.612(2)	11.163(1)
b/Å	9.620(2)	11.226(2)	11.220(2)	12.268(2)
c/Å	22.288(3)	22.396(2)	22.466(3)	21.505(3)
β/deg	95.19(1)	99.79(1)	99.71(2)	96.06(1)
Unit cell volume/Å^3	2665(1)	2867.8(6)	2885(1)	2928.7(6)
Z	4	4	4	2
d_{calcd}/g cm^{-3}	1.29	1.20	1.23	1.30
μ(Cu $K\alpha$/mm^{-1}	2.29	2.12	2.15	2.20
Collected reflcns	4433	4624	4649	4719
Unique reflcns	4218	4499	4524	4584
R_{int}	0.010	0.012	0.037	0.012
Observed reflcns, m	3345 ($F \geq 3\sigma(F)$)	3226 ($F \geq 3\sigma(F)$)	3148 ($F \geq 3\sigma(F)$)	3583 ($F \geq 3\sigma(F)$)
Transmission coeff	0.88/1.00	0.77/1.00	0.71/1.00	0.84/1.00
No. of variable, n	317	326	344	344
$R^{a)}$	0.057	0.057	0.064	0.053
$R_w{}^{b)}$	0.074	0.081	0.079	0.065
GOF$^{c)}$	1.574	1.476	1.553	1.240
Final residual/e Å^{-3}	0.63 −0.24	0.88 −0.28	0.37 −0.30	0.51 −0.26

a) $R=\sum||F_o|-|F_c||/\sum|F_o|$, b) $R_w=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{1/2}$, c) $\mathrm{GOF}=[\sum w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$.

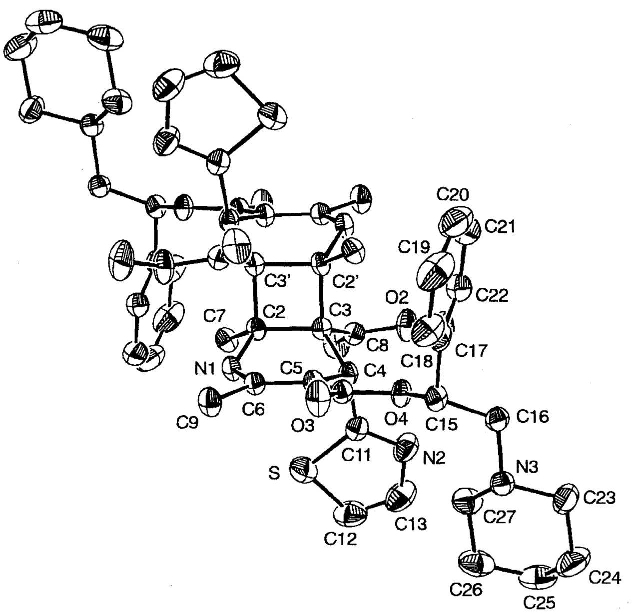


Fig. 1. Molecular structure of **4** showing the labeling scheme and the 40% probability ellipsoids. The two half molecules are related by the crystallographic center of symmetry. Chloride ions and water molecules are omitted for clarity.

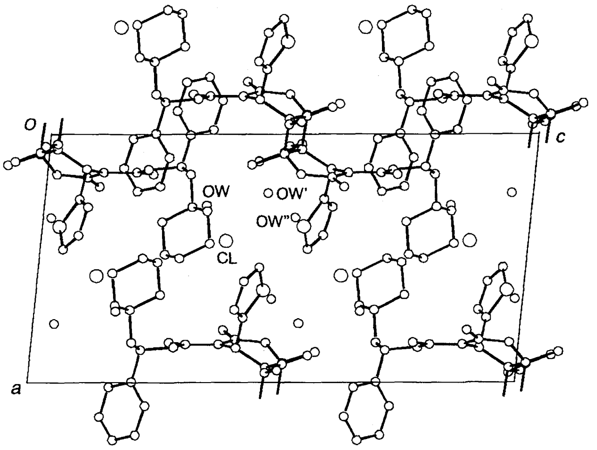


Fig. 2. Packing diagram of **4** viewed down the *b* axis. OW, OW′, and OW″ represent the incorporated water molecules.

with the 4-(2-thiazolyl) group in a pseudoaxial orientation. The bond distance of the cyclobutane ring connecting the two halves is significantly long (1.611(4) Å), presumably due to the highly crowded conformation around the cyclobutane ring. These structural features of **4** are quite similar to those of the photodimer (**2**) of compound **1**.[6)]

Photolysis of the dimer **4** under the same conditions as those for **3** was performed in order to examine the reversibility of the solid-state photochemical transformation between **3** and **4**. It was found that **4** is quite photostable, and no formation of **3** was observed. The irradiation of UV light at a wavelength below 320 nm also resulted in a 100% recovery of **4**. Thus, the solid-state photochemical transformation between **3** and **4** is not reversible. A methanol solution of **4** (0.1%), however, afforded **3** in 99% yield upon UV irradiation (300 nm) for 4 h.[10)]

Crystal Structures of Polymorphs. According to Schmidt's topochemical rule, the reacting double bonds should be close (ca. 4 Å) and nearly parallel in the crystal structure for photodimerization.[2)] Thus, X-ray analyses of the three crystal forms were performed to obtain the precise geometrical parameters of the crystal structures of the starting material for topochemical arguments and inspections of the circumstances surrounding the reaction site. The molecular structure of form I is depicted in Fig. 3. Selected geometrical parameters for form I are listed in Table 2. The dihydropyridine moiety adopts the conformation commonly observed for 4-aryl-1,4-dihydropyridine derivatives,[6,11)] i. e. the flat-boat conformation with the 4-(2-thiazolyl) group in a pseudoaxial orientation. In the crystal structure of form I there is no short intermolecular contact between the dihydropyridine rings, as shown in Fig. 4. Thus, the arrangement of the molecules in the crystal of form I does not conform to Schmidt's rule, and is consistent to the photostability.

The molecular structure of form II is similar to that of form I, as shown in Fig. 5 and Table 2. The crystal structure of form II is depicted in Fig. 6. In this crystal structure the double bonds in the dihydropyridine rings related by the center of symmetry are parallel with a center-to-center distance of 4.054(6) Å and a short displacement of 0.82(1) Å. The geometrical parameters describing the relative orientation of two double bonds in the crystal are defined in Scheme 2,

Table 2. Selected Bond Distances, Bond Angles and Torsion Angles for **3** (Forms I, II, and III) and **4**

	Form I	Form II	Form III	**4**
Bond distances (Å)				
N1–C2	1.382(4)	1.382(6)	1.386(6)	1.470(3)
N1–C6	1.381(4)	1.376(5)	1.369(5)	1.359(3)
C2–C3	1.353(5)	1.350(6)	1.347(6)	1.562(4)
C3–C4	1.515(4)	1.516(6)	1.517(6)	1.568(4)
C4–C5	1.513(4)	1.519(6)	1.513(6)	1.513(4)
C5–C6	1.356(5)	1.357(6)	1.356(6)	1.364(4)
C2–C3′	> 8.0[a)]	4.054(6)[a)]	4.042(6)[a)]	1.611(4)
Bond angles (deg)				
C2–N1–C6	122.1(3)	123.3(4)	123.3(4)	125.2(2)
N1–C2–C3	118.4(3)	118.8(4)	119.1(4)	111.5(2)
C2–C3–C4	118.4(3)	120.0(4)	119.8(4)	114.0(2)
C3–C4–C5	109.7(3)	110.8(3)	110.9(3)	112.9(2)
C4–C5–C6	118.5(3)	119.0(3)	119.4(3)	117.8(2)
N1–C6–C5	118.5(3)	119.2(4)	119.1(4)	119.0(2)
C3–C2–C3′	—	78.3(3)[a)]	80.1(3)[a)]	89.5(2)
C2–C3–C2′	—	101.7(3)[a)]	99.9(3)[a)]	90.5(2)
Torsion angles (deg)				
C6–N1–C2–C3	20.6(5)	16.4(7)	16.6(7)	30.4(4)
C2–N1–C6–C5	−22.8(5)	−13.5(7)	−13.5(7)	−29.4(4)
N1–C2–C3–C4	11.5(5)	6.3(6)	5.6(6)	4.9(3)
C2–C3–C4–C5	−36.9(4)	−28.0(5)	−26.8(5)	−37.3(3)
C3–C4–C5–C6	34.7(4)	30.7(5)	29.7(5)	41.9(4)
C4–C5–C6–N1	−7.3(5)	−11.9(6)	−11.4(6)	−10.1(4)

a) Non-bonded distances and angles.

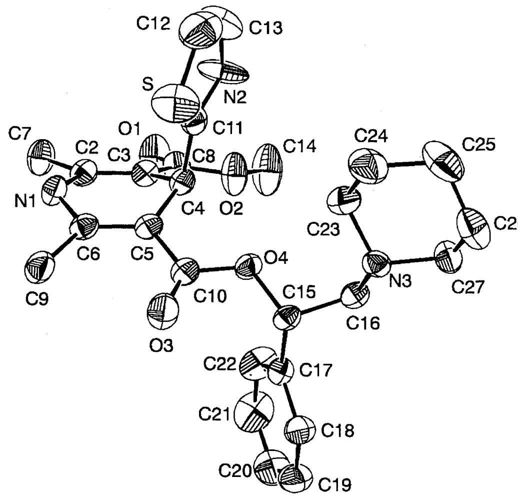


Fig. 3. Molecular structure of **3** in form I showing the labeling scheme and the 50% probability ellipsoids.

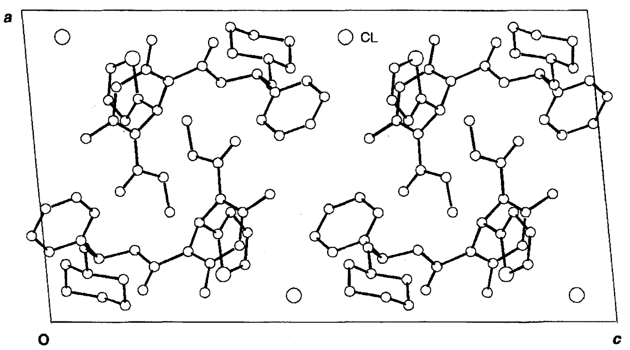


Fig. 4. Packing diagram of form I viewed down the *b* axis.

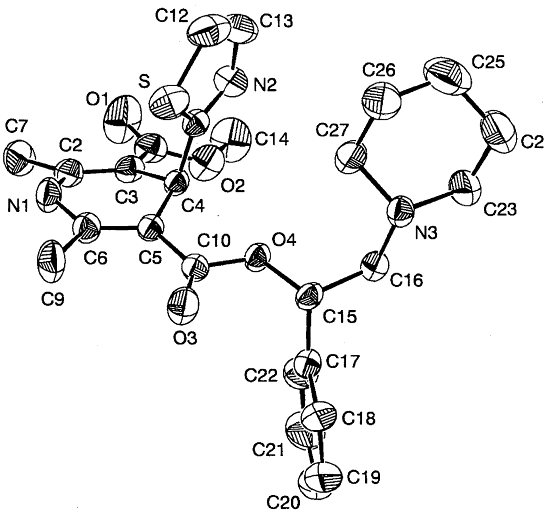


Fig. 5. Molecular structure of **3** in form II showing the labeling scheme and the 50% probability ellipsoids.

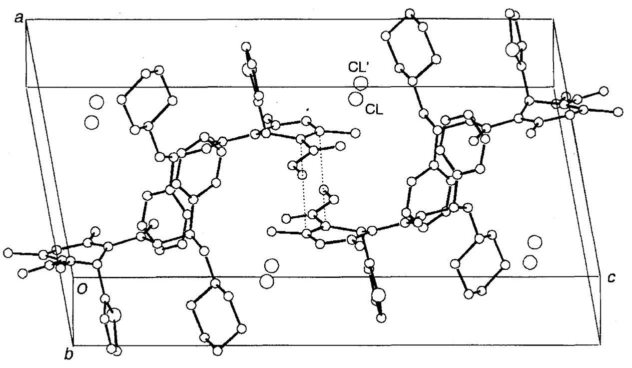
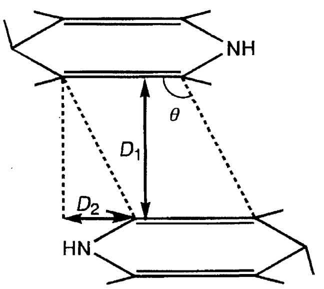


Fig. 6. Packing diagram of form II. The dashed lines represent the routes for photodimerization.



Scheme 2.

Table 3. Relative Orientations of the Double Bonds for **1** and **3** (Forms II and III)

	$D_1{}^{\mathrm{a)}}$(Å)	$D_2{}^{\mathrm{b)}}$(Å)	$\theta^{\mathrm{c)}}$(deg)
Form II	4.054(6)	0.82(1)	78.3(3)
Form III	4.042(6)	0.69(1)	80.1(3)
1$^{6)}$	3.728(6)	0.14(1)	87.8(3)
Ideal value	< 4.2	0.0	90.0

a) D_1: center-to-center distance between double bonds, b) D_2: displacement of double bonds along the double-bond axis, c) θ: angle of parallelogram formed by double bonds.

and are listed in Table 3. The data obviously show that the molecules in the crystal of form II can be photoreactive and could afford the centrosymmetric photodimer **4**. It should be noted that the unit cell volume of form II is significantly larger than that of form I (Table 1) and the position of the chloride ion is disordered over two sites in the crystal of form II (CL···CL′ 0.90(1) Å). This indicates that the packing of form II is much looser than that of form I.

The crystal structure of form III is almost identical to that of form II and the position of chloride ion in form III is disordered over two sites (CL···CL′ 0.906(9) Å), as shown in Fig. 7. Selected geometrical parameters of the molecule and the geometrical parameters describing the relative orientation of double bonds for form III are listed in Tables 2 and 3, respectively. The data indicates that the molecules in the crystal of form III should also be equally photoreactive as form II, according to Schmidt's rule. Thus, the remarkable difference in photoreactivity between forms II and III should be ascribed to the presence of water molecules in the crystal. Further, these data clearly demonstrate that the proximity and orientation of the double bonds in the crystal are important and predominant factors for the photodimerization of 1,4-dihydropyridines; however, other factors must be necessary to execute the reaction efficiently in the crystalline state. As shown in Fig. 7, the water molecule is located near the chloride ion (CL···OW 3.19(2), CL′···OW 2.55(2) Å) and

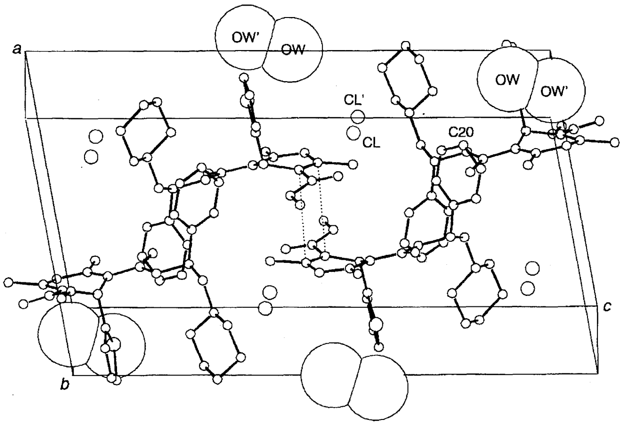


Fig. 7. Packing diagram of form III. The dashed lines represent the routes for photodimerization. The disordered oxygen atoms of the water molecule, OW and OW′, are shown with the van der Waals radius.

is disordered over two sites (OW···OW′ 1.92(3) Å) in the crystal of form III. There is no intermolecular hydrogen bond between molecules of **3** and water molecules, indicating that the water molecules are loosely packed in the crystal of form III in which they may have a space-filling role. This is consistent with the ease of interconversion, i.e. dehydration and rehydration, between forms III and II, as described before.

It is well known that most solid-state photodimerizations proceed heterogeneously with the destruction of the parent crystal phases, although several examples of crystal-to-crystal (homogeneous) photodimerization have been reported.[12] When a single crystal of form II was irradiated, a gradual decay of the crystal surface was observed, indicating that the dimerization proceeds heterogeneously. This is consistent with the fact that the packing modes of the crystal structures before and after the reaction are different (Figs. 6 and 2). In the case of bulky olefins, not only atoms near to the reacting double bond, but also peripheral atoms, should move in the crystal for photodimerization, as described in the previous paper.[6] Thus, it is considered that the photodimerization of bulky olefins proceeds heterogeneously, and cannot occur readily.

Relationships between Crystal Structures and Photoreactivity. Many 4-aryl-1,4-dihydropyridines have been synthesized so far as calcium channel antagonists. Typically, they possess bulky substituents on the dihydropyridine ring and their solid-state photodimerization seems to be an unlikely event. In fact, solid-state photodimerization of 4-aryl-1,4-dihydropyridines has never been reported. We discovered, however, that 4-aryl-1,4-dihydropyridines can photodimerize in the crystal.[6] It was the first example of the solid-state photodimerization of 4-aryl-1,4-dihydropyridines. We pointed out that 4-aryl-1,4-dihydropyridine can dimerize under the conditions governed by two controlling factors: a) proximity and orientation of the double bonds in the crystal (Schmidt's rule) and b) the space in the crystal to afford mobility of the monomer molecules (buffer zone). The remarkable difference in the photoreactivity between forms II and III in this study is also explained in terms of the buffer zone, as follows.

Forms II and III are isomorphous and the arrangements of molecules in the crystals are the same. The only difference between the two forms is the presence of water molecules in form III. In the highly photoreactive crystal structure of form II, an extra space is available for the mobility of the molecules for dimerization, whereas the space is occupied by water molecules, which prevent the movement of reactants in the less-photoreactive form III. In order to confirm this and to inspect the environment around the water molecules of form III, the crystal structure of form III and the dimer molecule (**4**) were superimposed. Although the dimer molecules can be placed in the crystal structure of form III, as shown in Fig. 8(b), the distance between the phenyl ring of the dimer and the water molecule is quite short (the distance between C20 of the dimer and OW is ca. 2.6 Å), which prevents the approach of the two molecules. This steric hindrance must be the reason for the markedly reduced photoreactivity in this form. On the contrary, the dimer molecule can be placed in a highly photoreactive crystal structure of form II without any short contacts with the surrounding molecules (Fig. 8(a)). The space where the water molecule is incorporated in form III apparently constitutes the buffer zone in form II that could buffer the steric hindrance caused by the approach of the molecules during the dimerization process. Thus, monomer molecules can approach each other to dimerize by using the buffer zone in the crystal.

Photochemical and crystallographic studies on **1**[6] and **3** show different aspects of the buffer zone in the crystal for photodimerization. The buffer zone in the crystal of **1** is a space formed by a conformational disorder of the molecule. On the other hand, the buffer zone in the crystal of **2** is a space

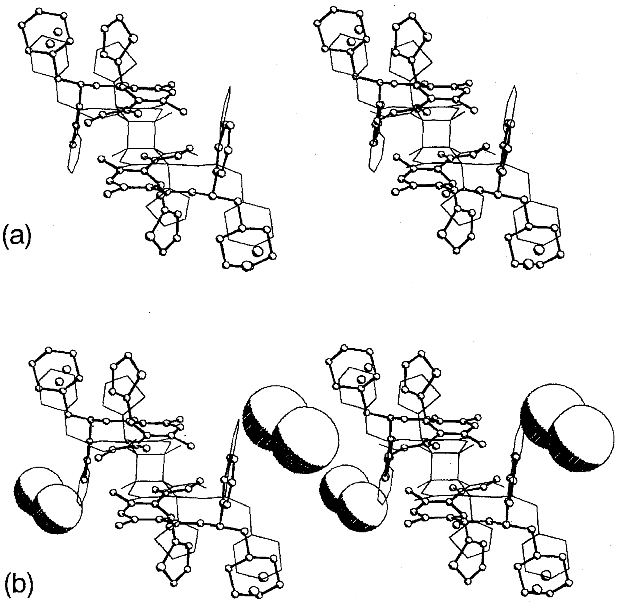


Fig. 8. Molecular arrangement near the reaction sites in forms II (a) and III (b). The ball-and-stick and the stick models represent the monomer and the dimer molecules, respectively. The disordered oxygen atoms of the water molecule are shown with the van der Waals radius.

where water molecules can be incorporated, and the reactivity for dimerization is controlled by the existence of water molecules in the crystal. The fact that the photodimerization of **1** proceeds much faster than that of form II of **3**[13)] may be related to the difference in the type of the buffer zone and/or the geometrical prerequisite governed by Schmidt's rule; all of the parameters (D_1, D_2, and θ) for form II of **3** given in Table 3 are apparently more unfavorable than those of **1** for photodimerization. In both cases, however, the buffer zone is observed as a disorder in the crystal; it is not located near to the reacting double bonds, but at the position where the movement of peripheral atoms is required for dimerization. As in the cases of **1** and **3**, 4-aryl-1, 4-dihydropyridines can dimerize by using the buffer zone in spite of their bulkiness. The formation of a buffer zone, disorder in the crystal, is normally unexpected and undesirable to obtain high-quality crystals, but must be an important factor for photodimerization of bulky olefins in addition to Schmidt's rule. The concept of the buffer zone must be very important to help in the molecular design of photoreactive crystals.

Experimental

Materials and Methods. Methyl (*RS*)-1-phenyl-2-piperidinoethyl (*RS*)-1,4-dihydro-2,6-dimethyl-4-(2-thiazolyl)pyridine-3,5-dicarboxylate hydrochloride (**3**) was synthesized at Yoshitomi Pharmaceutical Industries Ltd., (Japan). Spectral measurements were carried out using the following equipment: Shimadzu UV-2500 PC (UV), JEOL GSX400 (^{1}H and ^{13}C NMR), and JEOL DX300 (mass spectrum). An elemental analysis was performed on a YANACO MT-3 CHN corder. A TG analysis was performed on a SEIKO I & E, TG/DTA 20. HPLC analyses were carried out using a Shimadzu LC10AD pump equipped with a Shimadzu SPD6A UV detector and a C-R6A data processor. The conditions were as follows: column, Shimadzu STR ODS-II 4.6 mm i.d. ×150 mm; mobile phase, 0.05 mol dm^{-3} perchlorate buffer (pH 2.5)–acetonitrile (1 : 1); flow rate, 1.0 ml min^{-1}; detection, UV at 263 nm.

Photolyses. Photolyses were performed at room temperature using a Nagano Science LT-120 irradiator equipped with a Toshiba chemical lamp FIR-20S-BL/M (800 μW cm^{-2}) or a JASCO CRM-FA spectro irradiator. The crystalline samples were packed between two glass plates and placed in an irradiator. The time course of reaction was checked by HPLC periodically. Irradiation of form II of **3** for 8 h afforded photoproduct **4** in 58% yield. An analytical sample was obtained by recrystallization from methanol–water as colorless crystals, mp 213—214 °C. Found: C, 54.37; H, 6.51; N, 7.35%. Calcd for $C_{52}H_{62}N_6O_8S_2\cdot 2HCl\cdot 6H_2O$: C, 54.58; H, 6.69; N, 7.34%. UV (methanol) $\lambda_{max} = 304$ ($\varepsilon = 29640$), 270 ($\varepsilon = 14820$), 243 ($\varepsilon = 13816$) nm. FAB-MS: *m*/*z* 963 ([M+1]$^+$). ^{1}H NMR (0.005 M HCl/D$_2$O, 70 °C, 400 MHz, M = mol dm^{-3}) $\delta = 7.57$ (1H, d), 7.40—7.50 (6H, m), 6.05 (1H, dd), 4.85 (1H, s), 3.76 (1H, dd), 3.44 (3H, s), 3.33 (1H, br. d), 3.24 (1H, br. d), 2.87 (1H, br. t), 2.74 (1H, br. t), 2.18 (3H, s), 1.50—1.80 (5H, m), 1.75 (3H, s), 1.35 (1H, m). ^{13}C NMR (0.005 M HCl/D$_2$O, 70 °C, 100 MHz) $\delta = 174.88$, 172.83, 168.88, 161.98, 142.69, 139.19, 131.93, 131.64, 129.22, 123.97, 99.97, 73.22, 69.78, 63.49, 62.11, 56.62, 56.55, 54.70, 44.37, 25.08, 23.18, 23.02, 20.94.

Single-Crystal X-Ray Analyses. Single crystals of **4** were obtained by slow evaporation from water–methanol. Single crystals of forms I and II were grown by slow evaporation from acetonitrile and ethanol–ethyl acetate, respectively. Attempts to grow single crystals of form III were unsuccessful because crystals were not grown under a high relative humidity of more than 50%. A single crystal of III was prepared by leaving the single crystal of form II to stand at ca. 70% RH for 1 week.

All X-ray data were collected on an Enraf–Nonius CAD4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Crystal data and details of the structure determinations are given in Table 1. The unit cell parameters were obtained from a least-squares refinement using the setting angles of 25 reflections in the range $40° < \theta < 45°$. Intensity data were collected at room temperature using the ω–2θ scan mode to a maximum θ value of 60°. Three standard reflections were monitored every 120 min of exposure time. The data were corrected for Lorenz and polarization, but not for absorption. Independent reflections with $F > 3\sigma(F)$ were used in structure solution and refinement. The structures were solved by direct methods using MULTAN 11/82[14)] and subsequent Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms bonded to nitrogen atoms were located from difference Fourier maps. All other hydrogen atoms, except those of solvent molecules, were calculated geometrically. The coordinates of all hydrogen atoms were fixed. The structure were refined by full-matrix least-squares using the MolEN system,[15)] and weights were applied in the final cycles of refinement according to the scheme $w = (\sigma F^2 + 0.0004F^2 + 1)^{-1}$. For forms II and III, the chloride ion was found to be statistically distributed over two positions, and were located with 0.8 and 0.2 site occupancies, respectively. The water molecule of form III was found to be statistically distributed over two positions, and both of them were located with 0.5 site occupancy. The atomic coordinates, thermal parameters, bond distances and angles, and $F_o - F_c$ data have been deposited as Document No. 71008 at the Office of the Editor of Bull. Chem. Soc. Jpn.

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