Discrimination in the Solid-State Photodimerization of 1-Methyl-5,6-diphenylpyrazin-2-one

Menahem Kaftory,*[a] Vitaly Shteiman,[a] Tali Lavy,[a] John R. Scheffer,[b] Jie Yang,[c] and Volker Enkelmann[d]

Keywords: Chirality / Crystal structure / Enantioselectivity / Photochemistry / Solid-state reactions

1-Methyl- and 1-ethyl-5,6-diphenylpyrazin-2-one crystallize in two modifications, one of which is light-stable and the other light-sensitive. The light-sensitive modification is known to undergo photodimerization in the solid state. This polymorph crystallizes in the monoclinic space group $P2_1$ with two crystallographically independent molecules in the asymmetric unit. The molecules are packed in stacks running parallel to the unique *b* axis. The two independent molecules are arranged alternately along the stack. In principle, there are two different pairs of molecules within a stack that can undergo photodimerization, and each should form a different enantiomer. A large crystal was irradiated and a solution of the product was separated by HPLC. The optical purity of the (+)-enantiomer sample was estimated to be greater than 90 %. This finding indicates that only one of the two pairs undergoes photoreaction. The structure of a single crystal of the pyrazinone was elucidated by X-ray diffractometry before and after irradiation with a laser at a wavelength of 488 nm to 19 % conversion. The results of the crystal-structure determinations provide additional evidence that only one of the two pairs of molecules undergoes photodimerization although there are no significant differences between the distances between the reacting centers. Furthermore, the latter results suggest that weak hydrogen bonds are a dominant factor that determines which of the two pairs is dimerized upon irradiation.

Introduction

1-Methyl- and 1-ethyl-5,6-diphenylpyrazin-2-one are inert to photolysis in benzene or methanol solution; however, it has been reported that irradiation of the methyl derivative (**1**) in the solid state at 253 nm for 4 h results in the formation a [4 + 4] dimer.[1] In principle, four different cyclodimers may be anticipated (as shown in Scheme 1): The *anti-trans* isomer with an inversion center, the *anti-cis* isomer with twofold symmetry in the plane formed by the two bonds connecting the monomers, the *syn-trans* isomer with twofold symmetry perpendicular to the plane of the two bonds connecting the monomers, and the *syn-cis* isomer with mirror-plane symmetry. The solid-state photoreaction, however, led only to a single isomer, the *syn-trans* dimer.

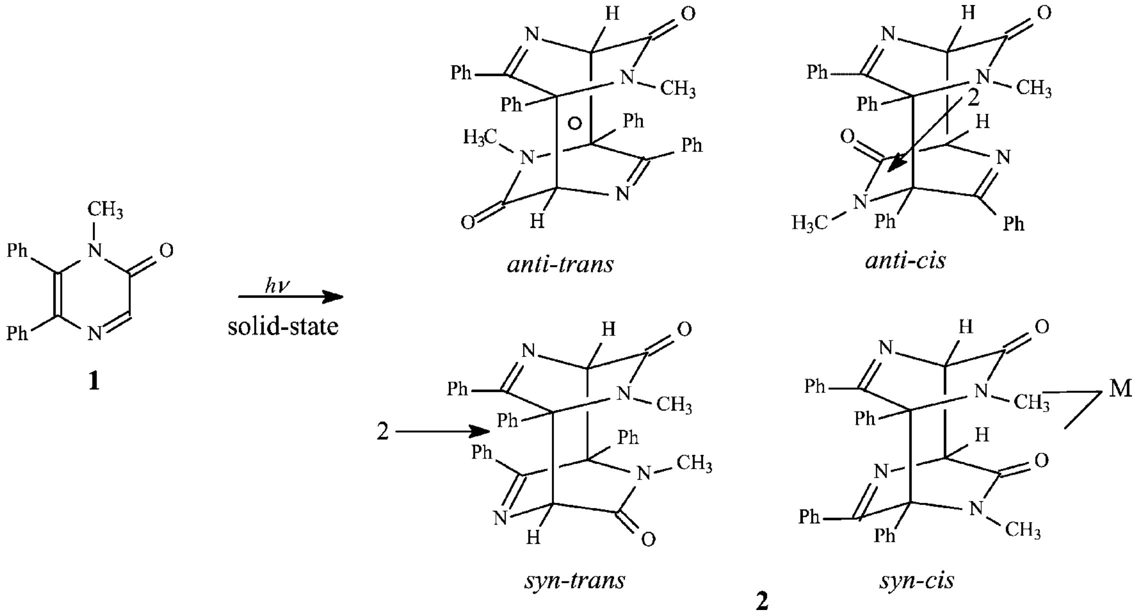
The solid-state photochemical dimerization of 1-methyl-5,6-diphenylpyrazin-2-one (**1**) was discussed in 1984 in two publications.[2,3] The compound crystallizes in two different polymorphic modifications: a light-sensitive form and a light-stable one. An interesting feature emerges from the crystal structure of the light-sensitive modification. This polymorph crystallizes in the chiral space group $P2_1$ with two crystallographically independent molecules in the asymmetric unit (see Figure 1). Since there is no stereogenic center in the molecule, the difference in the handedness between enantiomorphs is determined by the relative rotation of the phenyl substituents to the pyrazinone ring. It has long been recognized that the chemical transformation of a chiral crystalline specimen of one handedness into an optically active reaction product would constitute a novel asymmetric synthesis.[4] Extensive studies on solid-state photodimerization reactions of olefinic and related systems have shown that the space symmetry that relates two reactant molecules in the starting material uniquely dictates the point symmetry of the dimeric photoproduct.[5,6] It has been shown that in [2 + 2] cyclodimerization, if the pre-reacting molecules are related by a twofold axis parallel to the plane of interaction, an optically active product is formed.[6]

However, such solid-state photodimerizations are not common. If the monomers crystallize in isolated pairs, a

---

[a] Department of Chemistry, Technion - Israel Institute of Technology,
Haifa, Israel
Fax: +972-4829-5703
E-mail: kaftory@tx.technion.ac.il
[b] Department of Chemistry, University of British Columbia,
Vancouver, BC, Canada
[c] 3M Corporate Research Materials Laboratory,
3M center, Building 201–3N-04, St. Paul, MN 55144-1000, USA
[d] Max Planck Institute für Polymerforschung,
Mainz, Germany

DOI: 10.1002/ejoc.200400350



Scheme 1.

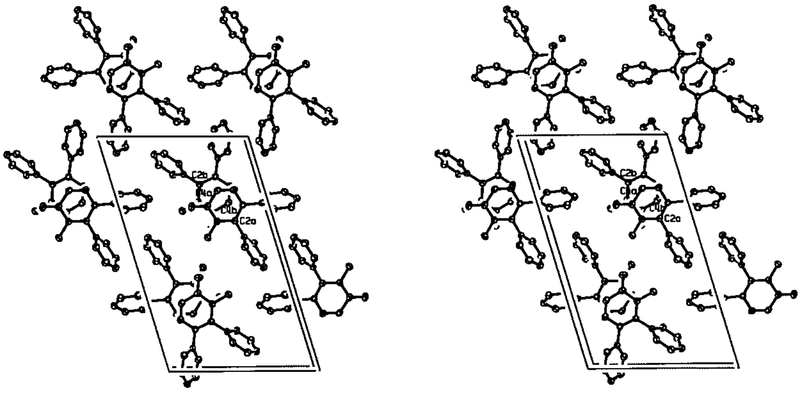


Figure 1. Stereoscopic view of the unit cell of pyrazinone **1** down the *b* axis, at 150 K

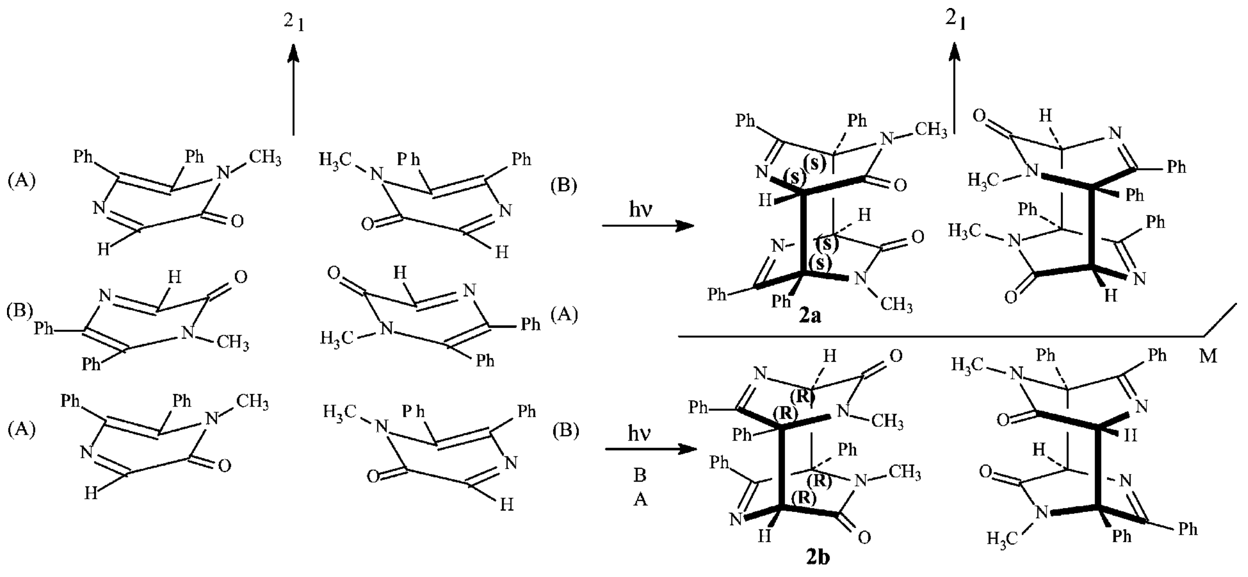
product with 100% optical yield is expected. If, on the other hand, each monomer has two potentially reactive neighbors, then either a racemate or a nonracemic mixture of enantiomers may be obtained. The last statement is valid for the photodimerization of **1** in the solid state. The molecules pack in stacks running parallel to the *b* axis. The two independent molecules in the asymmetric unit that are lying in the stack are related by a pseudo-twofold rotation axis perpendicular to the stack. The alternating arrangement of the two molecules enables photodimerization in two different ways, as shown in Scheme 2.

Irradiation of a single crystal of one handedness might lead to one of the following results: (a) the pairs (AB) will photodimerize and the dimer will be optically active with the configuration (*S*,*S*,*S*,*S*; see **2a** in Scheme 2); (b) the pairs (BA) will photodimerize and the other enantiomer would be obtained (*R*,*R*,*R*,*R*; see **2b** in Scheme 2); (c) both pairs will photodimerize and a racemic mixture will be obtained. A fourth possibility is unequal AB–BA photodimerization. Unfortunately, all attempts to find the absolute structure of photoproduct **2** by single-crystal X-ray diffraction methods failed. Replacement of the oxygen atom by a sulfur atom with the expectation that the pyrazinethione will be isomorphous with pyrazinone **1** and thereby enable the determination of the absolute structure failed as well. The pyrazinethione was found to be light-stable, with a different crystal structure from that of the pyrazinone.[7]

Alternative experiments leading to the discrimination between the possible courses of the photodimerization are described below.

Results and Discussion

The enantiomeric excess of the solid-state photoproduct **2** was determined by chiral HPLC. Crystals of pyrazinone **1** from one recrystallization batch were found to give the same enantiomer of photoproduct **2** upon solid-state photolysis. Since no racemic sample of product **2** could be obtained directly from the solid-state photolysis of pyrazinone



Scheme 2.

1, a nonracemic sample was prepared by mixing the (–)-enantiomer of photodimer **2** with the corresponding (+)-enantiomer. The corresponding HPLC trace for this sample is given in Figure 2. Another sample of the (+)-enantiomer of photodimer **2** was also injected onto the chiral HPLC column, and the trace is shown in Figure 3. It was found that the signal peak of the (+)-enantiomer of photodimer **2** is sharper than the signal peak of the (–)-enantiomer, but both enantiomers gave signals with long tails: no baseline separation of signals was achieved in this experiment. The estimated experimental error is less than 10%, and the optical purity of the (+)-enantiomer sample shown in Figure 3 is estimated to be greater than 90%. The optical rotation of this sample was measured as $[\alpha]_D = +208.0$ (at room temperature, in 10 mg mL^{-1} chloroform solution). The meaning of these surprising results is that the photodimerization of pyrazinone **1** is enantiospecific. These results are especially surprising in light of the geometrical information available from the crystal structure of pyrazinone **1** (see below). Since there are no significant differences between the distances of the reacting centers in both pairs, it is therefore important to find out which of the two possible pairs of molecules (AB) or (BA) photodimerize.

In a series of publications, Enkelmann and coworkers have described the use of irradiation in the long-wavelength tail of the absorption band for the study of solid-state photochemical reactions.[8–13] Under these irradiation conditions the solid-state photoreaction proceeds homogeneously through a solid solution of reactant and product over the entire range of conversion. Following these conditions and irradiating a single crystal of pyrazinone **1** to partial conversion one might obtain an insight into the photodimerization and distinguish between the possible reacting pairs. The ultraviolet spectrum of **1** in EtOH shows absorption maxima at 261 and 351 nm.[1] Accordingly, a single crystal of pyrazinone **1** was mounted for X-ray diffraction intensity measurements at low temperature. The diffraction intensities were measured at 150 K before and after irradiation by a laser at 488 nm. The results are summarized below.

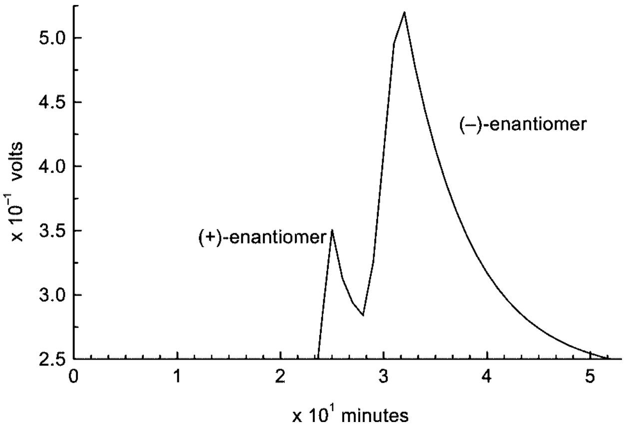


Figure 2. The HPLC trace of a nonracemic mixture of photodimer **2**

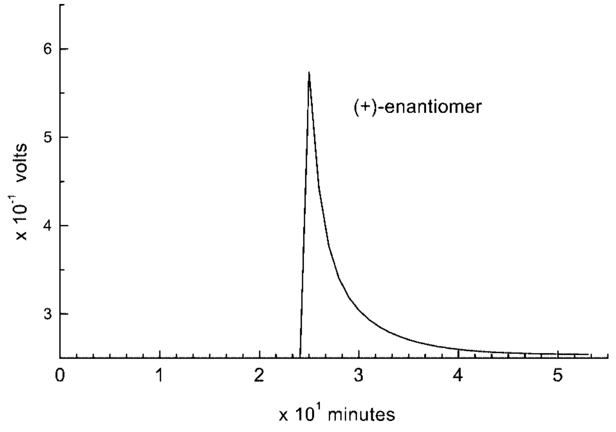


Figure 3. The HPLC trace of the (+)-enantiomer of photodimer **2**

Crystal Structure of Pyrazinone 1

The crystallographic data for pyrazinone **1** before and after irradiation are given in the Experimental Section. Fractional atomic coordinates, anisotropic atomic displacement parameters, and tables of bond lengths and angles have been deposited (see note in the Experimental Section). A stereoscopic view of the unit cell at 150 K before irradiation is shown in Figure 1.

The molecules are packed in stacks running parallel to the *b* axis. The two independent molecules within a stack are related to each other by a pseudo-twofold rotation axis running parallel to the central ring plane. There are two nonidentical pairs of molecules along the stack, denoted as (BA) and (AB). The pair denoted as (BA) consists of molecules whose central rings are lying at $y = -0.25$ and 0.25, respectively (see Figure 4 top) and the pair denoted as (AB) consists of molecules whose central rings are lying at $y = 0.25$ and 0.75, respectively (see Figure 4 bottom). The two independent molecules are practically parallel [the angle between their central ring mean plane is 2.43(1)°]. Therefore, the mutual orientation and lateral displacement of the two independent molecules in each pair within the stack are practically equal (see Table 1). The geometry of the reaction centers of the two different pairs is very similar (see Figure 4). The distances between the reacting atoms are practically the same (the largest difference is 0.06 Å): C2a···C4b = 3.500(3), C4a···C2b = 3.505(3) Å in the pair (AB), and C2b···C4a = 3.505(3), C4b···C2a 3.566(3) Å in the pair (BA).

Table 1. Comparison of interatomic distances [Å] between the central rings of the two pairs (BA) and (AB); the distances between the reacting atoms are in bold

	(BA)	(AB)
O1a···C5b	3.324(2)	3.294(2)
C5a···O1b	3.369(2)	3.325(2)
N1a···C1b	3.374(3)	3.245(3)
C1a···N1b	3.356(3)	3.241(3)
N2a···C3b	3.530(3)	3.751(3)
C3a···N2b	3.569(3)	3.743(3)
C2a···C4b	**3.566(3)**	**3.500(3)**
C4a···C2b	**3.505(3)**	**3.505(3)**
Σ	27.593	27.604

Crystal Structure of the Irradiated Crystal of Pyrazinone 1

The irradiated crystal is a homogeneous solid solution consisting of 81% unreacted monomer and 19% of the product dimers (see Figure 5). For atomic notation see Figure 4 and Figure 6. The crystal lattice of the parent compound is not affected by the formation of the solid solution, therefore the space group remains $P2_1$. The most significant change in the molecular geometry resulting from the dimerization is the variation of the hybridization of atoms C2 and C4 (of the two independent molecules) from sp^2 to sp^3, followed by

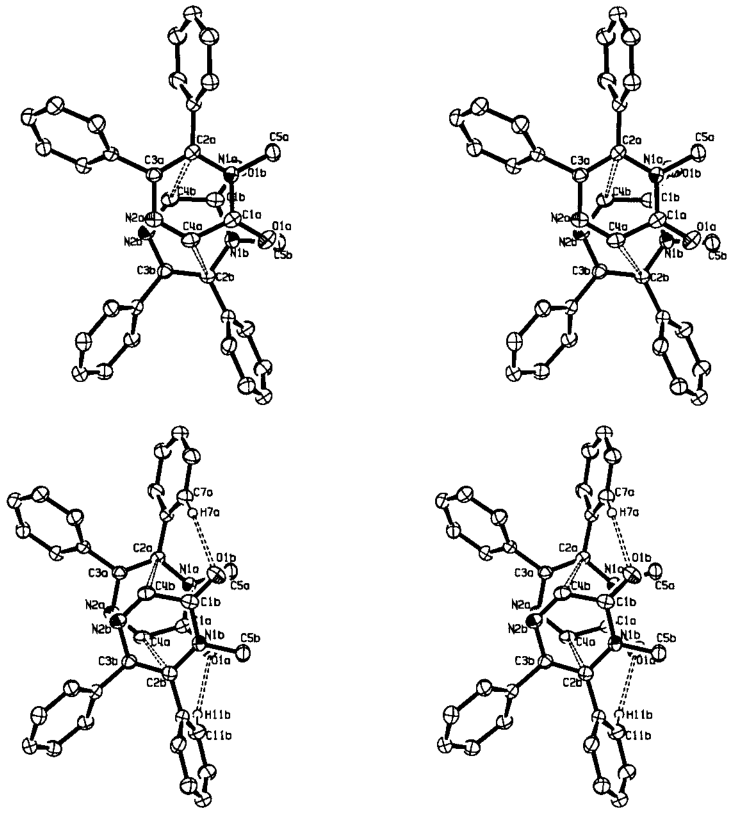


Figure 4. Stereoscopic view of the two pairs (BA, top) and (AB, bottom); hydrogen atoms have been omitted for clarity; the broken lines are drawn between the atoms that will be bonded to form the dimer, and dashed lines represent hydrogen bonds

a conformational change of the central six-membered ring from planar to a boat. The formation of the dimer was observed by the accumulation of electron density between C2 of one molecule and C4 of the other. The refinement details are given in the Experimental Section. *The electron density was detected only between the molecules of the pair (AB).* No electron density was found between the molecules of the pair (BA). This implies that, upon irradiation, only the pairs of type (AB) photodimerize. The structure of the dimer is shown stereoscopically in Figure 6. As a result of the dimerization the phenyl rings are shifted and rotated compared to the structure of the monomer. The relative rotations range between 7.16° (C6a–C11a, C6c–C11c) and 10.22° (C12a–C17a, C12c–C17c).

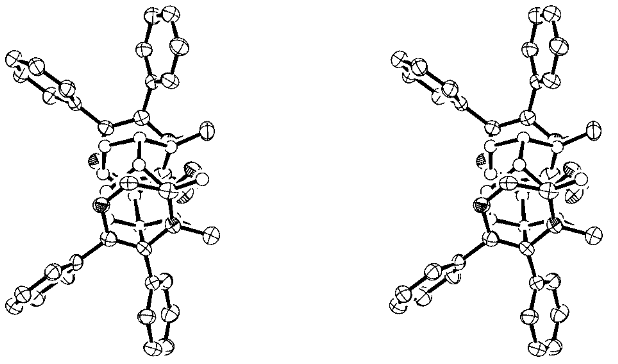


Figure 5. Stereoscopic view of the dimer (19% marked by circles) within the monomer (81%); the phenyl rings of the dimer have been omitted for clarity

As mentioned above, one of the nonbonding distances between the photoreactive centers (C4a···C2b) is equal (3.505 Å) in the two pairs (AB) and (BA); the second nonbonding distance (C2a···C4b) differs by 0.061 Å.[14] It is hard to believe that such a small difference is the reason for the discrimination between the two pairs. The answer to the question of why the reaction takes place between the pair of molecules denoted as (AB) and not between the pair of molecules denoted as (BA) is attributed to the two C=O···H–C hydrogen bonds that exist in (AB) but not in

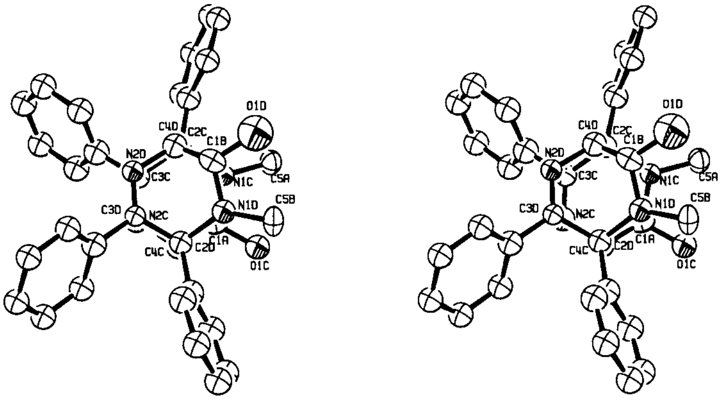


Figure 6. Stereoscopic view of the dimer

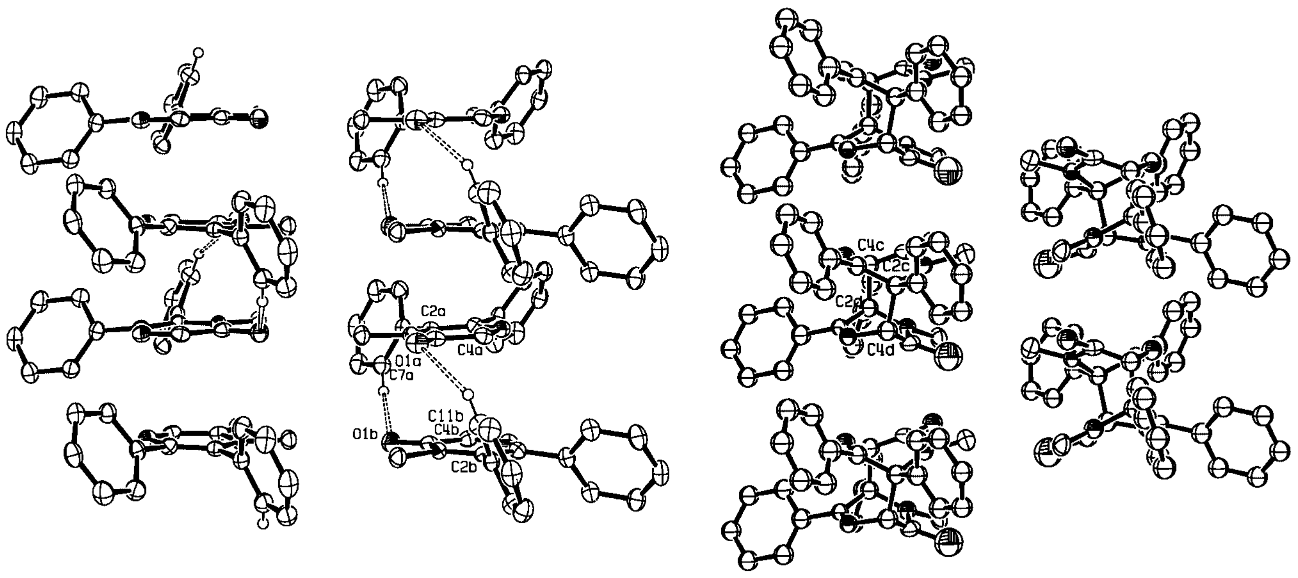


Figure 7. Left: two stacks of the monomer related by a screw axis showing the hydrogen bonds; right: the stacks after irradiation, showing the dimers

(BA). The geometry of these hydrogen bonds is as follows: O1b···H7a = 2.487(3) Å, O1b···C7a = 3.364(3) Å, O1b···H7a–C7a = 157.3(3)°, and O1a···H11b = 2.560(3) Å, O1a···C11b = 3.447(3) Å, O1a···H11b–C11b = 155.0(3)°; the closest intermolecular O···H distances in (BA) are O1a···H7b and O1b···H11a [3.708(3) and 3.527(3) Å, respectively]. The hydrogen bonds hold the two molecules together, thus facilitating the photochemical reaction (see Figure 7).

The position of the hydrogen atoms of the dimer could not be located; however, the distances between the oxygen atoms and carbon atoms involved in the hydrogen bonding do not vary significantly: O1b···C7a = 3.487 Å, and O1a···C11b = 3.515 Å. These results imply that hydrogen bonding is essential for the discrimination during the photodimerization.

Conclusions

We have carried out the single-crystal irradiation and crystal-structure determination of three different crystals and found that in these cases a photodimer is formed between the two molecules that are held together by hydrogen bonds. It should be noted, however, that the experiments were performed on a single crystal. One cannot rule out the possibility that crystals of the monomer having the opposite chirality will photodimerize to the dimer of the opposite handedness. Therefore the main conclusion of this work is that intermolecular interactions can be dominant in the determination of photoproduct.

Experimental Section

Preparation of the Materials: Commercially available reagents were purchased from Aldrich and used without further purification. Thin-layer chromatography (TLC) was carried out using aluminium sheets precoated with silica gel 60F (Merck 5554). The plates were inspected under UV light. Column chromatography was carried out using silica gel 60F (Merck 9385, 0.040–0.063 mm). Infrared spectra were recorded with a Nicolet Impact 400 Fourier transform spectrometer using KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded (at room temperature) with a Bruker Avance 200 spectrometer (200 MHz), using residual solvent as the internal standard. All chemical shifts are quoted on a δ scale, and all coupling constants (J) are expressed in Hertz (Hz). Samples were prepared using $CDCl_3$ or [D$_6$]DMSO purchased from Aldrich.

2-Hydroxy-5,6-diphenylpyrazine: Sodium hydroxide (12.5 M, 3.2 mL 40 mmol) was added over 30 minto a refluxing mixture of glycine amide hydrochloride (2.2 g, 20 mmol), benzil (4.2 g, 20 mmol), and 50 mL of methanol. After refluxing for another 30 min, the mixture was treated with 2.5 mL of 12 M hydrochloric acid, followed by 2 g of solid potassium hydrogen carbonate. The yellow solid formed was filtered off, washed well with water, and recrystallized from *tert*-butyl alcohol. Yellow needles of 2-hydroxy-5,6-diphenylpyrazine were obtained after filtration (3.0 g; yield: 60%). M.p. 240–250 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3050–2500 (broad), 1657, 1588, 1562, 1496, 1438, 1376, 1228, 1163, 1026 cm^{-1}. MS: m/z (%) = 248 (100) [M$^+$], 229 (5), 219 (62), 165 (28). ^{1}H NMR ([D$_6$]DMSO, 200 MHz): δ = 12.25 (br. s, 1 H, OH), 8.18 (s, 1 H, 3-H), 7.30 (m, 5 H) ppm.

1-Methyl-5,6-diphenylpyrazine-2-one (1): Dimethyl sulfate (0.252 g, 2 mmol) was added dropwise at room temperature to a stirred solution of 2-hydroxy-5,6-diphenylpyrazine (0.5 g, 2 mmol) and sodium methoxide [formed from 64 mg (2 mmol) of sodium and 40 mL of methanol] and the reaction mixture was refluxed for 1 h. The solution was then concentrated under reduced pressure, poured into 10% HCl solution, and extracted with dichloromethane. The extract was washed in turn with 10% $NaHCO_3$ solution and water and dried with anhydrous magnesium sulfate. After removal of the of the solvent, the residue was chromatographed with diethyl ether and petroleum ether (50:50, v/v) to give **1** (0.4 g; yield: 76%), which was recrystallized from ethanol to afford yellow prisms. M.p. 165–167 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3027, 1646 (C=O), 1578, 1556, 1483, 1442, 1414, 1319, 1241, 1185, 1155 cm^{-1}. MS: m/z (%) = 262 (74) [M$^+$], 233 (100), 218 (11), 165 (66), 118 (32), 89 (42), 77 (45). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 8.30 (s, 1 H, 3-H), 7.42–7.12 (m, 10 H), 3.32 (s, 3 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 200 MHz): δ = 156.09 (C=O), 146.54 (3-C), 138.59, 137.40, 133.85, 132.11, 129.90, 129.67, 129.17, 129.12, 127.81, 127.12, 33.80 (CH_3) ppm.

(1α,2α,5α,6α)-3,7-Dimethyl-2,6,10,12-tetraphenyl-3,7,9,11-tetraazatricyclo[4.2.2.2^{2,5}]dodeca-9,11-diene-4,8-dione (2): Photodimer **2** was isolated after the solid-state photolysis of pyrazinone **1**. A typical photolysis is given below: a single crystal of **1** (23 mg, 0.09 mmol) was photolyzed for 20 h with a medium-pressure mercury lamp equipped with a Pyrex filter. The resulting solid was dissolved in a small amount of ethyl acetate, and the photodimer **2** was isolated by column chromatography with 20% diethyl ether in petroleum ether (v/v). Recrystallization from ethyl acetate gave colorless needles (17 mg; yield: 74%). M.p. 148–150 °C. IR (KBr): $\tilde{\nu}_{max}$ = 3058, 2967, 1657 (C=O), 1494, 1446, 1423, 1387, 1266, 1098, 1039, 1001 cm^{-1}. MS: m/z (%) = 262 (100), 233 (82), 165 (83), 118 (90), 89 (79), 77 (90). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 7.35–6.85 (m, 20 H), 6.30 (s, 2 H), 2.52 (s, 6 H, CH_3) ppm.

Determination of Enantiomeric Excess: The enantiomeric excess of the solid-state photoproduct **2** was determined by chiral HPLC Chiral Column: Chiralcel OD, Chiral Technologies Inc. Detector: UV detector at λ = 261 nm. Solvents: 2-propanol 1%, hexane 90%. Flow Rate: 1 mL min^{-1}.

Irradiation: The irradiation system consisted of an Osram Xe short-arc lamp (150 W) using a commercial glass filter that blocks light of wavelengths lower than 450 nm. A single crystal of pyrazinone **1** was attached with grease to a thin piece of glass connected to a solid piece of metal, and mounted on a device that revolved at 1 rpm. The crystal was irradiated for 6 h. Similar results were obtained with a laser at 488 nm. A single crystal was cooled during the irradiation for 3 h.

Crystal-Structure Determination and Refinement: Details of crystallographic data collection and crystal structure determination are given in Table 2. The refinement procedure of the irradiated crystal needs some comments. After locating the atomic positions of the dimer, the refinement proceeded as follows: the site occupancy of the atoms belonging to the monomer was refined as a free variable, which, after refinement, converged at 0.81 for the monomer (0.19 for the dimer). All the atoms of the dimer were refined isotropically, and the phenyl rings were refined as rigid groups. The absolute structure of the crystal of the monomer and of the dimer could not be assigned. The diffractometer intensities were collected with a Nonius KappaCCD diffractometer. The software programs used for data collection and reduction were KappaCCD[15] and DENZO SMN;[16] for structure solution and refinement SHELXS-97 and SHELXL-97;[17] and for graphic presentations ORTEP-3 for Windows.[18] CCDC-216315 (for the monomer) and CCDC-216316 (for the dimer) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The research was partially supported (M. K.) by the Fund for the Promotion of research at the Technion, and by the Technion V.P.R Fund.

Table 2. Crystallographic details.

Parameter	**1** (monomer)	**1** + **2** (dimer)
Formula	$C_{17}H_{14}N_4$	$C_{17}H_{14}N_4$
Mol. mass	262.30	262.30
Crystal color, habit	yellow, prism	yellow, prism
Crystal dimensions	0.30 × 0.20 × 0.2	0.30 × 0.20 × 0.2
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$P2_1$
a [Å]	18.658(5)	18.510(7)
b [Å]	6.466(2)	6.466(5)
c [Å]	11.535(4)	11.542(4)
α [°]	90.00	90.00
β [°]	107.03(3)	106.17(5)
γ [°]	90.00	90.00
V [Å^3]	1330.6(1)	1326.8(1)
Z	4	4
$D_{\text{calcd.}}$ [g cm^{-3}]	1.309	1.313
μ(Mo-K_α) [cm^{-1}]	0.083	0.083
F(000)	552	552
2θ max [°]	58.28	55.14
Reflections collected	3863	3110
Independent reflections	3863	2507
Observed reflections	3329	3110
Largest difference peak [e Å^{-3}]	0.234	0.293
Largest difference hole [e Å^{-3}]	–0.170	–0.248
No. of parameters	109	438
R[a]	0.0397	0.0635
wR[a]	0.0934	0.2554
GOF[b]	1.048	1.048

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [b] GOF = $[\Sigma w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$, where NO is the number of observations and NV is the number of variables.

---

[1] T. Nishio, N. Nakajima, Y. Omote, *Tetrahedron Lett.* **1980**, *21*, 2529–2530.
[2] M. Kaftory, *J. Chem. Soc., Perkin Trans. 2*. **1984**, 757–765.
[3] T. Nishio, N. Nakajima, M. Kondo, Y. Omote, M. Kaftory, *J. Chem. Soc., Perkin Trans. 2* **1984**, 391–396.
[4] K. Hoogsteen, *Acta Crystallogr.* **1963**, *16*, 28–38.
[5] G. M. J. Schmidt, *Pure Appl. Chem.* **1971**, *27*, 647–678.
[6] B. S. Green, M. Lahav, G. M. J. Schmidt, *Mol. Cryst. Liq. Cryst.* **1975**, *29*, 187–200.
[7] A. B. Zolotoy, M. Botoshansky, M. Kaftory, J. R. Sheffer, J. Yang, *Acta Crystallogr., Sect. C* **2002**, *58*, 220–222.
[8] V. Buchholz, V. Enkelmann, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1998**, *313*, 309–314.
[9] K. Novak, V. Enkelmann, W. Koehler, G. Wegner, K. B. Wagener, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1994**, *242*, 269–276.
[10] V. Enkelmann, G. Wegner, K. Novak, K. B. Wagener, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1994**, *240*, 121–126.
[11] K. Novak, V. Enkelmann, G. Wegner, K. B. Wagener, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1614–1616.
[12] K. Novak, V. Enkelmann, G. Wegner, K. B. Wagener, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 510–511.
[13] V. Enkelmann, G. Wegner, K. Novak, K. B. Wagener, *J. Am. Chem. Soc.* **1993**, *115*, 10390–10391.
[14] S. K. Kearsley, *Organic Solid-State Chemistry* (Ed.: G. R. Desiraju), Elsevier Science publishers, Amsterdam, **1987**, pp. 69–115.
[15] Nonius, *COLLECT*, Nonius BV, Delft, The Netherlands, **2000**.
[16] Z. Otwinowski, W. Minor, in *Methods in Enzymology*, vol. 276 ("Molecular Crystallography"), part A (Eds.: C. W. Carter, Jr., R. M. Sweet), Academic Press, New York, **1997**, pp. 307–326.
[17] G. M. Sheldrick, *SHELXS-86* and *SHELXL-97*, University of Göttingen, Germany, **1997**.
[18] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

Received: May 19, 2004