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Investigation of the Origin of the Topochemical Arrangement in Photoreactive 2-Benzyl-5-benzylidenecyclopentanone Crystal

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Investigation of the origin of a dimeric pair structure of the title compound molecules in a crystal was extensively conducted. Molecular dynamics calculations suggested that conventional van der Waals and electrostatic estimations did not accurately reproduce the temperature dependence of the interatomic distance of the dimeric pair, as observed in X-ray structure analyses. A dimeric pair formation of the monomer in a solution was also observed by spectroscopic studies. X-ray structure analysis of a photodimer crystal revealed that the packing motif of the monomer crystal is quite similar to the dimer crystal. It is speculated that, on crystallisation from a solution, the monomer molecule form a dimeric structure near the crystal surface and make a stack similar to the dimer crystal.

Keywords: single-crystal-to-single-crystal; photodimerisation; X-ray structure analysis; molecular dynamics; electronic spectroscopy

INTRODUCTION

Most 2+2 photocycloaddition reactions take place when double bonds are parallel and approximately 4Å apart, requiring minimal structural change to achieve the dimerisation. This is well-known as the 'Schmidt rule'[1]. However, why molecules adopt such a favourable configuration in crystals has not been well-investigated.

Single crystals of 2-benzyl-5-benzylidenecyclopentanone (BBCP) undergo such a topochemical, single-crystal-to-single-crystal reaction when irradiated with UV light, yielding the photodimer (Figure 1).[2]

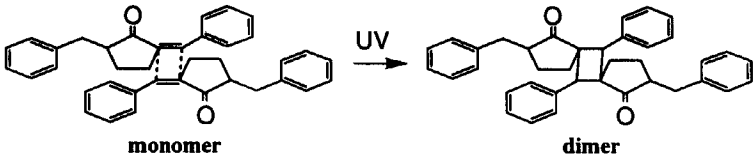

FIGURE 1. Photodimerisation of 2-benzyl-5-benzylidene-cyclopentanone (BBCP).

In the monomer crystal, two adjacent molecules related by the crystallographic inversion centre face each other, forming a dimeric structure (Figure 2). The thin solid lines which connect the C5...C13^{i} (*i*; symmetry operation of [-*x*, 1-*y*, -*z*]) and C13...C5^{i} atoms in Figure 2 indicate that new covalent bonds are formed by the reaction.

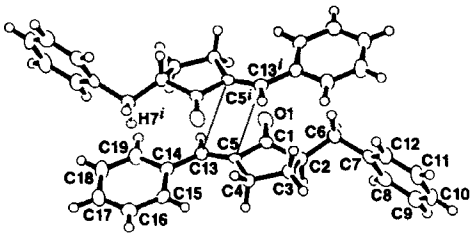

FIGURE 2. Pair configuration in the monomer crystal.

In previous papers[3,4], we suggested that the change in the C5...C13^{i} intermolecular distance in association with temperature is strongly related to the temperature dependence of the photodimerisation reaction rate. The rate constant increases linearly as the temperature increases to ~200 K, yielding an activation energy of ~13 kJmol^{-1}. Surprisingly, the rate constant *decreases* above this threshold temperature. The intermolecular distance of the two reacting carbon atoms, C5 and C13^{i}, was kept at a constant value of 4.15 Å under the threshold temperature of ~200 K. Above it, the intermolecular distance expanded as the temperature increased. No apparent crystal phase transition was observed around the threshold temperature. We have speculated that the reaction is dominated by thermal vibration of the lattice below the threshold temperature, while above it the reaction is likely to be dependent on the expanding intermolecular carbon-carbon distance. Such special temperature dependence of the intermolecular distance should depend on the intermolecular interactions between the adjacent monomers. Thus our next interest has been focused on understanding the origin of the molecular arrangement which exhibits such an interesting temperature dependence.

Here, we analyse the intermolecular interactions by using a computational chemistry method. We have also investigated using spectroscopic methods whether the monomers adopt a dimeric structure in solution. In addition, from a comparison of the structure of a recrystallised dimer crystal to that of the as-formed dimer crystal obtained by the photoreaction, we hypothesise that the monomers form the dimeric structure bound by intermolecular interactions and act like the dimer when they are crystallised.

RESULTS AND DISCUSSION

Molecular dynamics (MD) simulation

If the intermolecular interactions in the monomer crystal are sufficiently estimated in terms of conventional potential function and parameters, MD simulations should reproduce a temperature dependence of the C5...C13^{i} distance similar to that observed in the previous X-ray analysis; the temperature dependence should show an inflection point around ~200K. We performed MD simulations by using the Cerius2 package at different temperatures. The result was negative. In Figure 3 the temperature dependence obtained by the simulation is compared with that obtained by the X-ray study. In the simulation data, no inflection point was found and the C5...C13^{i} intermolecular distance simply expanded as the temperature increased.

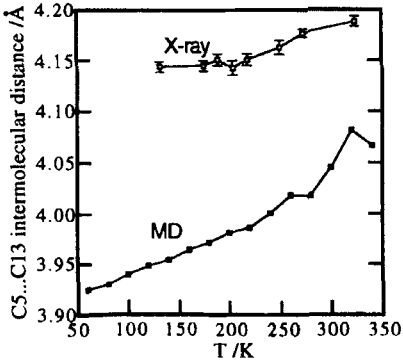

FIGURE 3. Comparison of the C5...C13^{i} distances.

In the MD simulation, conventional intermolecular interactions such as van der Waals interaction and electrostatic interactions were taken into account. Hydrogen bonds were not considered as no close O...H intermolecular contacts were observed in the crystal structure. We argue that the present potential functions and parameters are not accurate

enough to sufficiently reproduce the intermolecular interactions working in the BBCP crystal. In the crystal structure, we have found close C...H intermolecular contacts between the aromatic carbon atoms C14, C15, C16, C17, C18, and C19 and the aliphatic hydrogen atom H7^{i} (3.03(4), 3.15(4), 3.31(4), 3.36(4), 3.23(4) and 3.08(4)Å, respectively, at 132K), suggesting CH/π interactions[6] between the two molecules. Another weak intermolecular interaction, the π-π interaction, could be considered as existing between the C5...C13^{i} olefin bonds. Those weak intermolecular interactions must be comprehensively explained with further accurate estimation of their interaction energies.

Spectroscopic study on BBCP monomer in solution

In order to evaluate the intermolecular interactions in solution, the absorption and fluorescence spectra of the BBCP monomer were measured in acetonitrile. The absorption spectra revealed the main peak at 298 nm. In addition, a weak band around 340-400 nm was observed in a high concentration range above 10^{-3}molL^{-1}.(Figure 4)

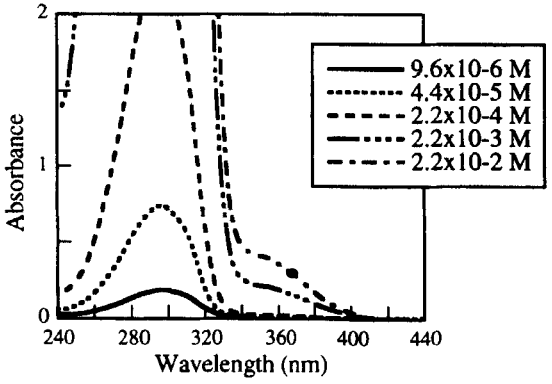

FIGURE 4. Absorption spectra of BBCP monomer in acetonitrile

The new absorption band may be due to an intermolecular overlapping state of the dimeric structure; that is, a dimeric complex of the monomers is formed at the high concentration. A similar weak absorption band has been observed in a cyclohexane solution, which has been interpreted as an n -› π^* transition.[7]

In the fluorescence spectra, we observed excitation peaks at 230 and 273 nm with the emission maximum of 330 nm. It should be mentioned that the wavelengths of the excitation maxima are shorter than that of the absorption maximum. A possible interpretation could be that the BBCP monomers form an excimer.

In summary, these electronic spectra strongly suggest that the BBCP monomers form a dimeric structure in solution when the concentration is high.

X-Ray structure analysis of recrystallised BBCP photodimer.

The crystal structure of the BBCP photodimer has been determined from an as-formed dimer crystal which was obtained by the photo-irradiation of a UV light on a monomer crystal.[2] Its packing motif is quite similar to the monomer crystal. This indicates that the dimer is packed under topochemical control of the monomer lattice. One should note that such an as-formed crystal phase would provide a relatively unstable one for the dimer molecule itself. We recrystallised the photodimer from a chloroform/methanol solution. The recrystallisation should allow the molecule to pack in the most favourable manner. We solved the crystal structure of the newly obtained crystal and compared it to the as-formed crystal. Table 1 compares the crystal data of the recrystallised dimer with those of the as-formed dimer crystal and the monomer crystal as well. It is revealed that they have almost identical crystal structure to each other. This means that the as-formed dimer crystal adopts the most stable crystal-phase for the dimer molecules. The monomer is also stacked in a manner similar to the photodimers. In other words, the starting monomer crystal is already constructed under

the most favourite packing mode to the BBCP dimer. Thus the starting monomer lattice is almost maintained during the photoreaction and atom movement in the reaction is minimal. Therefore, the single-crystal-to-single-crystal transition is achieved with very slight loss of the crystal integrity.

TABLE 1. Comparison of crystal data in BBCP crystals.

	monomer	as-formed dimer	recrystallised dimer
Formula	$C_{19}H_{18}O$	$C_{38}H_{36}O_2$	$C_{38}H_{36}O_2$
Formula weight	262.35	524.70	524.70
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Pbca*	*Pbca*	*Pbca*
a/Å	31.354(1)	31.307(5)	31.424(5)
b/Å	10.805(1)	10.810(2)	10.765(2)
c/Å	8.689(1)	8.644(5)	8.661(4)
V/Å^3	2943.6(4)	2925(2)	2930(1)
Z	8	4	4
Dx/Mg m^{-3}	1.184	1.192	1.189
Diffractometer	Nonius CAD4	Nonius CAD4	Nonius CAD4
Radiation	Mo*Kα*	Mo*Kα*	Mo*Kα*
Temperature/K	298	297	296

CONCLUSION

We hypothesise that, on crystallisation, the BBCP monomers form a dimeric structure near the crystal surface, where the concentration of the solution is high. We have observed a dimeric pair formation in a monomer solution by the spectroscopic study. The monomer molecules act like the dimer, which gives rise to the dimer-like arrangement. Thus the structure of the monomer crystal is quite similar to that of the most stable crystal phase of the dimer.(Figure 5) This should be the reason why the BBCP system shows a very stable single-crystal-to-single-crystal reaction. The MD simulation with conventional van der Waals and electrostatic potentials did not reproduce the temperature dependence of the interatomic distance of the dimeric pair in the

monomer crystal. Further accurate estimation of the intermolecular interaction energies is now progressing by using *ab initio* molecular orbital calculations.

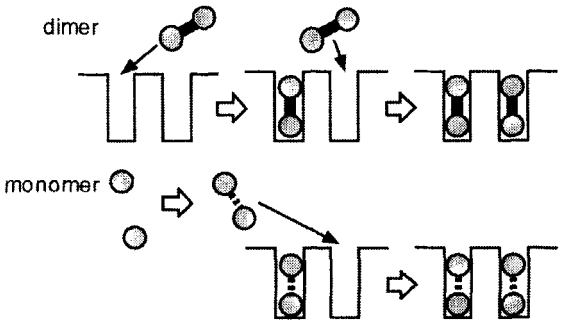

FIGURE 5. Proposed packing modes in BBCP crystals.

EXPERIMENTAL

Molecular dynamics simulation

The MD calculations were performed using a Cerius2 version 3.5 program package (Molecular Simulation Inc.). The cell parameters and atomic positions in the model were obtained from the crystal structure at 132K[4]. A large super-lattice unit cell was constructed with 1 x 2 x 3 original monomer unit cells in order to accurately estimate the long-range interactions in the MD calculation. The original *Pbca* symmetry was reduced to *P*1 symmetry to allow each molecule to move independently. Point charges were distributed on the monomer atoms by using the Electrostatic Potential Fitting method[8] based on HF/6-311G** level estimation. The force field parameters used were from the Universal Force Field 1.02[5]. The MD simulation starting with the prepared super-lattice structure was carried out with a time interval of 1 fs for the NPT ensemble using the Ewald reciprocal space sum to calculate energy and force contribution. The external pressure was set to

0.1 MPa. The system was equilibrated initially by a 5-ps simulation. The temperature was then raised by 20 K and the equilibration was performed again. This procedure was repeated over a temperature range of 20-360K. At each temperature in a range of 60-360K, a 40-ps simulation was carried out starting with the corresponding equilibrated structure. The structural parameters were obtained by averaging those data in a range of 10.2-40.0 ps with a 0.2-ps sampling interval.

Spectroscopic study of BBCP monomer in solution

Acetonitrile solutions of BBCP monomer were prepared with concentrations raging 10^{-6}-10^{-2} $molL^{-1}$. Absorption and fluorescence spectra were measured using a Shimadzu UV-2500 PC spectrophotometer and a Jasco FP-777 fluorescence spectrophotometer, respectively.

Preparation of BBCP photodimer

A powder of BBCP monomer synthesised according to the method described in the literature[9] was well-moulded and suspended in an aqueous solution in a quartz vessel. The suspension was continually stirred and irradiated by a 500W mercury lamp. The vessel was held in an ice-water to prevent the temperature from raising. At a constant interval a small portion of the suspension was sampled and dissolved in tetrahydrofuran and the UV spectra were monitored using a Shimadzu UV-2500 PC spectrophotometer. After 3 hour irradiation the spectrum showed no change and the photodimerisation reaction was judged complete. The suspended powder was filtered and dried, followed by recrystallisation from ethyl acetate to yield colourless transparent flakes, m.p. 242-244° (lit.[9], 242.5-243.5°), one spot t.l.c. (chloroform and ethyl acetate-ethanol).

X-ray structure analysis of recrystallised BBCP photodimer

The crystal data and experimental details are summarised in Table 1. The single crystal of the BBCP photo-dimer with dimensions of 0.52 x

0.41 x 0.06 mm^3 was prepared by vaporisation from a chloroform-methanol solution. Data collection was carried out using a Rigaku AFC-7R diffractometer with graphite-monochromated Mo$K\alpha$ radiation. Intensities were corrected for absorption using a ψ-scan method and for the Lorentz and polarisation factors. Three standard reflections measured at a constant interval showed a slight decay of 1.6% and no correction was applied. The structure was solved by a direct method (*SIR*92[10]) and refined by full-matrix least-squares on F using the *TEXSAN* program[11]. All the hydrogen atoms were located using difference Fourier maps and refined isotropically. Anisotropic thermal parameters were assumed for all the non-hydrogen atoms. Atomic scattering factors were taken from *the International Tables for X-Ray Crystallography Volume C.*

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