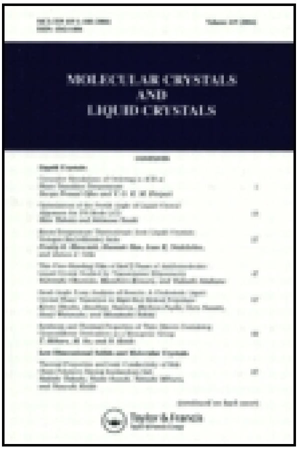

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Photoreactive Crystals: Photodimerization of a Diolefinic Derivative Accompanied by Isomerization

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The novel photoreactive crystal, 4-(4-(2-(ethoxycarbonyl)vinyl)-cinnamoylamino)benzoic acid, (ECAB) was prepared and its photoreactivity evaluated. By introducing an amide group into a p-phenylenediacrylic acid derivative, a "tape" structure network was constructed. On irradiation the crystals were converted into dimers quantitatively. Characterization of the dimer and the results of X-ray crystallographic analysis showed that photodimerization proceeds with selective cycloaddition of olefinic bonds on the "amide side" only and accompanied by trans-cis isomerization of an olefinic bond on the "ester side".

Keywords: p-phenylendiacrylic acid derivative; hydrogen bond; amide moiety; photodimerization; cycloaddition; isomerization

INTRODUCTION

Developing a molecular design stratergy for novel reactive organic solids is an important and challenging discipline. Solid state reactions are attractive systems because of high selectivity of reaction process, high yield, mild conditions and occasionally it can provide a unique molecular and crystals structure of compound which is difficult to prepare by conventional solution methods.

We have investigated photoreactions of a variety of olefinic compounds and have revealed the relationship between structure and photoreactivity.[1] Here we demonstrate the use of hydrogen bonding to dictate molecular packing and engineer functions such as photoreactivity and molecular recognition. We have prepared a series of diolefinic deivatives including an amide moiety and evaluated the role of hydrogen bonding relating to photoreactivity.[2] Among those compounds studied we have found that the crystals of the diolefinic compound, 4-(4-(2-(ethoxycarbonyl)vinyl)cinnamoylamino)benzoic acid, ECAB (1) undergoe a topochemical photodimerization with selective cycloaddition of olefinic bonds. ECAB has three hydrogen-bond acceptor sites (the acid, ester, amide carbonyl oxygen atoms) but only two hydrogen donors (acid O-H and amide N-H). The ECAB molecules adopt a hydrgen-bonded tape-like structure which leads to, upon photoreaction, a unique dimer with a cyclobutane ring carrying two olefinic bonds. The characteristics of this topochemical reaction including analysis of molecular packing, photoreaction process and molecular structure of the dimer product are presented below.

EXPERIMENTAL

Material

ECAB was prepared by condensation of p-aminobenzoic acid and chloride of p-phenylenediacrylic acid mono ethylester. It was purified by reprecipitation of ECAB dimethylsulfoixde solution with water. Mesophase was observed in temperature range of 255-312 °C. Elementary analysis; Calcd. for $C_{21}H_{19}NO_5$(%), C:69.03 H:5.24 N:3.83 Found, C:69.53 H:5.28 N:3.85 1H NMR(DMSO-d6, ppm)1.24 (t. methyl, 3H) 4.17(q. methylene, 2H) 6.65,6.88,7.62,7.62 (d. J= 16Hz, olefinic 4H)7.64-7.92(m. aromatic 8H) 10.55(s. carboxylic acid 1H)

Photoreaction

ECAB crystals (100 mg) were dispersed in water (100ml) with stirring and were irradiated with a 500-W Xenon lamp at room temperature. A cut-off filter (Corning Co. No.0-51) was used to irradiate the light with wavelength longer than 300 nm. Photoreaction process was followed by measuring the UV spectrum of irradiated crystals. After completion of reaction, the irradiated crystals were collected by filtration and dried in vacuo. The photoproduct was identified by UV, IR, NMR spectrum, elementary analysis and gel permeation chromatography. M.p. 270 °C Elementary analysis; Calcd for C42H38N2O10(%), C:69.03 H:5.24 N:3.87 Found, C:68.83 H:5.21 N:3.91 1H NMR(DMSO-d6, ppm) 1.10,1.22(t, methyl, 6H) 4.04,4.14(q. methylene, 4H) 4.10-4.20, 4.45-4.55
(m. cyclobutane, 4H) 6.53,7.60(d. J= 16Hz olefinic, 2H) 5.90,6.89 (d. J=13Hz olefinic 2H) 7.37-7.78(m. aromatic, 16H)

Measurement

UV spectrum was recorded with a Shimadzu UV-220 spectrophotomter and tetrahydrofuran was used as a solvent. IR spectrum was measured with a Perkin-Elmer System 2000 FTIR spectrometer. NMR spectrum was measured on a Varian Gemini-300BB NMR spectrometer.
Gel permeation chromatography (Shimadzu LC-5A) was employed using tetrahydrofuran as an eluent. Thermal analysis was carried out by using a differential scanning calorimeter (SEIKO I DSC-200) at a scanning rate of 5 °C/min. under nitrogen.

X-ray structure analysis

The single crystal of the ECAB photodimer with dimensions of 0.20 x 0.10 x 0.03 mm3 was prepared by vaporization from a tetrahydrofuran-ethanol solution. The crystal data are as follows: monoclinic space group *P2/c*, a = 20.36, b = 12.73, and c = 20.0 Å and β = 101.5°; V = 5079 Å^3; Dc = 0.95 gcm^{-3} for Z = 4 with $C_{42}H_{38}N_2O_{10}$.

Data collection was carried out using a Rigaku AFC-7R diffractometer with graphite-monochromated Cu$K\alpha$ radiation. The empirical absorption correction was applied. The structure was partially solved by a direct method, *SHELXS*86[3].

RESULTS AND DISCUSSION

ECAB has its absorption peak at 330 nm in solution (ε = 60000). In the solution trans-cis photoisomerization takes place slowly, while in the crystal high photoreactivity was confirmed by irradiation of the KBr pellet embedded ECAB crystal. After irradition for 1 hour, the UV spectrum of the irradiated crystals changed: the absorption peak (330 nm) shifted to shorter wavelength (282 nm) indicating that one of olefinic bonds disappeared by photoreaction. IR spectrum of the irradiated crystals indicated the decrease of intensity in the olefinic bond peak (1629 cm-1) leaving the olefinic bond peak (1634 cm-1) of ester side unreacted.[4]The results of gel permeation chromatography showed only one peak which suggests that the photoproduct consists of one kind of compound. Its molecular weight corresponds to that of a dimer judging from the calibration curve of standard polystyrene. These results indicate that there are almost no unreacted ECAB molecules in the photoproduct and the photoreaction proceeds quantitatively. The elementary analysis showed that the composition of elements of the photoproduct is the same as that of ECAB. Based on above data, it is concluded that the photoproduct is the dimer of ECAB. Further details of dimer structure were determined by NMR spectrum and the results of X-ray structure analysis. In NMR spectrum new peaks appeared at 4.10-4.20 and 4.45-4.55 ppm partly overlapping with peaks of methylene protons of ethyl group. Referring to the NMR spectrum data on cyclobutane ring protons,[5] the new peaks were assigned to be protons attached to a cyclobutane ring. The symmetrical patterns of these peaks also indicate that the dimer (2) has a head to tail structure as shown in FIGURE 1.

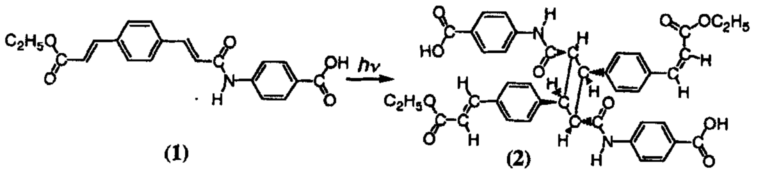

FIGURE 1 Photodimerization of ECAB in the crystalline state.

It should be noted that the other peaks such as methyl, methylene protons showed two kinds of chemical shifts and olefinic protons also have different chemical shifts with two kinds of coupling constants (J=16Hz, J=13Hz). These two kinds of chemical shifts for methylene and methyl protons are due to the presence of trans and cis olefinic bond in the dimer since the same kinds of chemical shifts were observed in NMR spectrum study of trans-cis photoisomerization of ethylester of cinnamic acid.[6] The presence of both trans and cis olefinic protons was confirmed by the values of coupling constant (J=16Hz for trans, J=13Hz for cis). According to NMR spectrum and X-ray structure analysis, ECAB molecule has only trans, trans olefinic bonds. It is concluded that trans to cis isomerization of olefinic bond takes place in one of two ECAB molecules during photoreaction process. As a result one olefinic bond is trans and the other is cis in the dimer (2).

The tape structure for ECAB monomer molecules is shown in FIGURE 2. The crystal structure has been determined previously.[2] It can be seen that the familiar 8-member carboxylic acid dimer is formed by hydrogen bonding. Each molecule is also involved in a second centrosymmetric dimer motif created by amide proton to ester carbonyl oxygen hydrogen bonds. There are no close contacts between olefinic bonds within the tapes. These molecules are almost planar and the distance between amide olefinic bonds of molecules in adjacent tapes is 3.83 Å which is within ractive distance. There is, however, no such close contact for the olefinic bonds in the ester side of molecule. Thus X-ray crystallography revealed that selective cycloaddition of amide olefinic bonds proceeds with ECAB molecules.

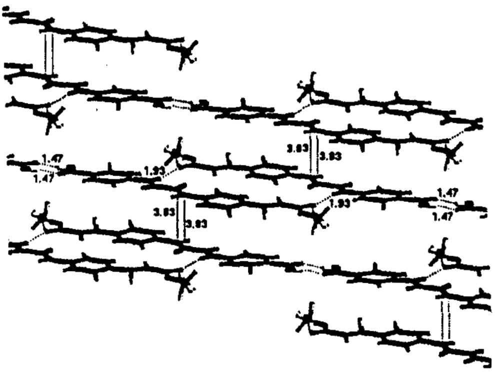

FIGURE 2 The tape type structure formed through hydrogen bonding for ECAB molecule.

It should be noted that ECAB analogue of compounds such as decyl ester and octadecyl ester are photostable. At present formation of single crystals of these compounds has not been achieved and structure analysis has not been carried out. However, it seems to be important for formation of tape network to design suitable chain length of an alkyl ester residue. There are a few reports for crystalline state photodimerization of diolefinic compounds.[6-9] One is a head to tail type cyclobutane dimer obtained from p-phenylenediacrylic acid diethylester and others are cyclophane type dimers. In these cases the yields of dimers are relatively low because their crystal packings are complicated and are not suitable arrangement for topochemical process.

In the present case use of hydrogen bond could succeed to lead to highly photoreactive tape network which provide a unique structure of the dimer with a high yield.

Figure 3 illustrates the molecular configuration of the ECAB photodimer determined by the X-ray structure analysis. Although the crystal structure has not been completely solved due to a disorder of the ethoxycarbonylethylene moiety of the ester side, it has been clarified that the cyclobutane ring is formed by the photo-cycloaddition of the olefinic bonds of the amide sides. The disorder strongly suggests that one of the olefinic bonds of the ester sides is isomerized from the trans form to the cis form.

In summary, a new photoreactive crystal with "tape" structure was prepared successfully using hydrogen bond. Topochemical photoprocess affords the unique dimer that is difficult to prepare by other conventional methods.

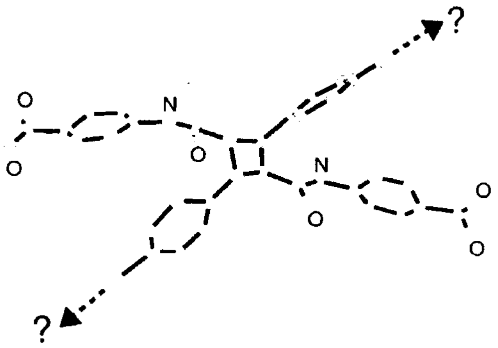

FIGURE 3 Molecular configuration of ECAB photodimer

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