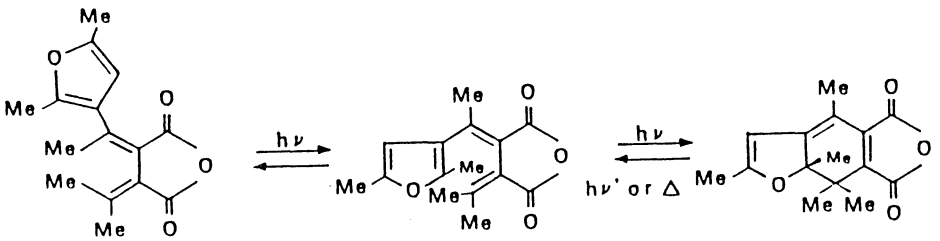
CHEMISTRY LETTERS, pp. 19-22, 1989.

Molecular and Crystal Structures of E- and Z-Isomers of 2,5-Dimethyl-3-furylethylidene(isopropylidene)-succinic Anhydride

Yasunori YOSHIOKA,* Takanori TANAKA,+ Masami SAWADA,+ and Masahiro IRIE*+
Central Research Laboratories, Kanegafuchi Chemical Industry Co. Ltd., 1-2-80 Yoshida-cho, Kobe 652
+The Institute of Scientific and Industrial Research, Osaka University, Ibaragi, Osaka 567

Molecular and crystal structures of E- and Z-isomers of 2,5-dimethyl-3-furylethylidene(isopropylidene)-succinic anhydride were examined. Both isomers have structures twisting between the furan ring and the succinic anhydride portion. The photocyclization reaction is initiated by a π-π^* transition from each part of the molecule, not from a π-orbital delocalized over the molecule.

It is well known that an E-form of 2,5-dimethyl-3-furylethylidene (isopropylidene)-succinic anhydride (3-furyl fulgide) undergoes a photocyclization reaction to produce a red colored closed form by irradiation with ultraviolet light and the closed form reverts to the E-form on exposure to visible light.[1-3] In addition, a Z-form of 3-furyl fulgide is converted to the closed form via the E-form on exposure to ultraviolet light. It has been suggested by Heller[4] that these types of fulgide compounds are useful as erasable optical memory materials because of their thermal stability.



The molecular and crystal structures of three isomers of 2-isopropylidene-3-[1-(2-methyl-5-phenyl-3-thienyl)ethylidene]succinic anhydride (3-thienyl fulgide) were published by Kaftory.[5] However, the relationship between the molecular structure and photochromic properties has not been well discussed. Therefore, we performed X-ray structure analysis of a typical 3-furyl fulgide in order to elucidate its photochromic properties.

3-Furyl fulgides were synthesized by the Stobbe condensation.[6] The E-isomer

and Z-isomer were isolated by using a column of silica gel. Each isomer was recrystallized from petroleum ether and obtained as pale yellow crystal. Crystals having the dimensions of 0.5 x 0.5 x 0.5 mm^3 were used for X-ray structure analysis. We tried to isolate the closed isomer by elution from thin-layer chromatography after the photocyclization reaction of the E-isomer in chloroform solution. The isolation was, however, unsuccessful. The closed form was not stable on the TLC plate and might decompose to other structures.

Rigaku AFC-5FOS was used to measure the X-ray diffraction of the single crystal of each isomer. 3538 Points were measured and independent 2335 points ($F > \sigma F$) were employed to analyze the molecular structure using MULTAN84 and Rigaku MBLS. R-factor was less than 10 percent.

Table 1 shows the crystal data of the E- and Z-isomers of 3-furyl fulgide. The crystal system of both isomers is monoclinic. The space group of the E-isomer is $P2_1/n$ possessing an inversion center and 2-fold spiral axis along the b-axis, while that of the Z-isomer is $P2_1/c$ possessing a 2-fold spiral axis along the b-axis and a glide reflection along the c-axis. The longest molecular axis of the E-isomer is parallel to the a-axis. The volumes of the unit cells of the E- and Z-isomers are quite similar, being 1371 $Å^3$ and 1339 $Å^3$, respectively. Four molecules are packed in the unit cell, a pair of two molecules being in a mirror image of the other.

It is interesting to compare the crystal system of the E-isomer of 3-furyl fulgide with that of the closed isomer of of 3-thienyl fulgide. Both isomers have same space group $P2_1/n$. The a- and b-axes of 3-furyl fulgide are 14.803 Å and 7.800 Å, which are quite similar to the values of 14.113 Å and 7.490 Å for the c- and b-axes of 3-thienyl fulgide. β angles are 109.29° and 106.59° for 3-furyl and 3-thienyl fulgides, respectively. These comparisons suggest that the crystal system of the closed form of 3-furyl fulgide is similar to that of the E-isomer.

The structural parameters of the E- and Z-isomers are summarized in Table 2. The numbering of each atom is shown in Fig. 1. First, we studied the molecular structure of the E-isomer. It can be seen in Table 2 that the bond sequence C10-C8-C1-C2-C9 consists of alternating single and double bonds. The bond distances of the double bonds C1-C8 and C2-C9 in the succinic anhydride portion are longer than those of the cis 1,3-butadiene, while the bond distance of single bond C1-C2 is shorter. Two bond angles C2-C1-C8 and C9-C2-C1 (132.1° and 131.2°) are quite large due to steric repulsion between the furan ring and the isopropylidene group, and are similar to those of 3-thienyl fulgide. Since two torsional angles C8-C1-C2-C9 and C3-C1-C2-C4 are -39.6° and -16.5°, respectively, the succinic anhydride portion deviates considerably from the planar structure. The degree of the distortion of the succinic anhydride portion coincides with that of 3-thienyl fulgide. On the other hand, the torsional angle of the furan ring is 1.6°, showing that the planar structure is retained in the molecule. The torsional angle -41.9° of C1-C8-C10-C12 , which corresponds to the linkage portion between the succinic anhydride and furan ring, slightly deviates from the value of 50° given in 3-thienyl fulgide. The distance between C9 and C12, which corresponds to the chemical bond formed in the closed form, 3.443 Å, is slightly shorter than the distance of thienyl fulgide, 3.9 Å. This may be due to the difference of

Table 1. Crystal data of two isomers of 3-furyl fulgide

	E-isomer	Z-isomer
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Cell dimension		
a(Å)	14.803(3)	8.375(2)
b(Å)	7.800(1)	7.627(2)
c(Å)	12.584(3)	21.153(4)
β(°)	109.29(1)	97.71(2)
V(Å^3)	1371	1339
Z	4	4
Dx(g/cm^3)	1.26	1.29
R	0.076	0.084

Table 2. Structural parameters of two isomers of 3-furyl fulgides. Distances in Å and angles in degree

	E-isomer	Z-isomer
C1 -C2	1.470(5)	1.452(10)
C1 -C8	1.361(5)	1.377(10)
C2 -C9	1.342(5)	1.352(10)
C8 -C10	1.470(4)	1.474(10)
C10-C12	1.355(4)	1.351(10)
C11-C13	1.326(5)	1.336(10)
C2 -C1 -C8	132.1(3)	129.4(6)
C1 -C2 -C9	131.2(3)	130.7(7)
C8 -C10-C12	128.1(3)	126.0(6)
C10-C12-C15	135.4(3)	135.3(7)

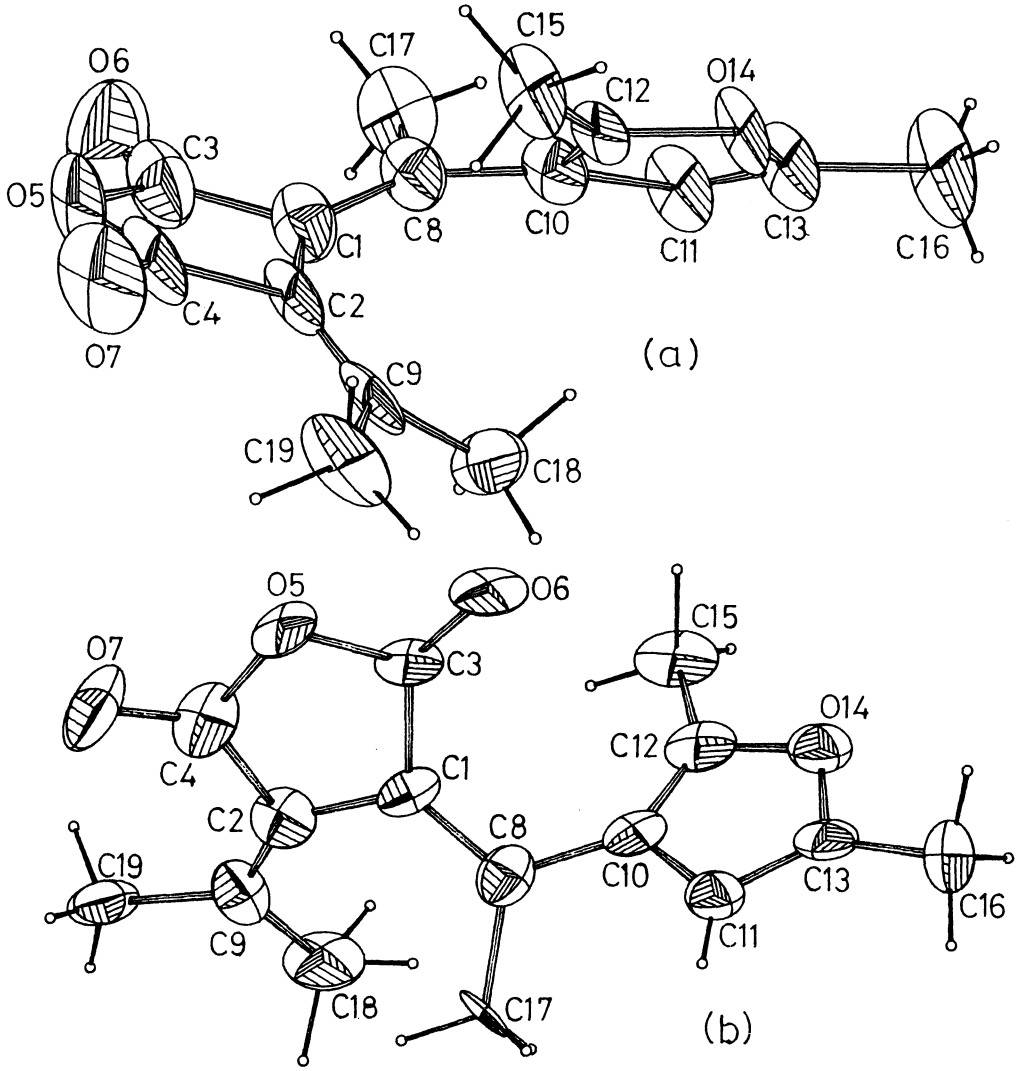


Fig.1. ORTEP diagrams of two isomers of 3-furyl fulgide with the atomic numbering. (a): E-isomer and (b): Z-isomer.

distortion between the succinic anhydride portion and furan ring. As can be seen from Fig. 1(a), it is concluded that the succinic anhydride and the furan ring are not coplanar and are considerably twisted relative to each other, as a result of the steric hindrance.

The molecular structure indicates that π-conjugation does not exist between the succinic anhydride and the furan ring. Heller et al. proposed that the photocyclization reaction occurs by n-π^* excitation of one of carbonyl chromophores in the molecule.[7] On the other hand, Becker et al. suggested that an excited singlet state having π-π^* character is responsible to the photochromic reaction.[8] The MNDO molecular orbital calculation[9] indicated that the molecular orbitals of the E-isomer are localized on each portion in the molecule, reflecting the distorted molecular structure, as obtained from the above X-ray analysis. The HOMO and the second HOMO of the E-isomer are bonding orbitals of π-character corresponding to the HOMO of the furan ring and the HOMO of the cis-butadiene of the succinic anhydride portion. The LUMO mainly consists of the π^*-antibonding LUMO of the cis-butadiene. The photoisomerization reaction is initiated by excitation between these orbitals. This is in good agreement with the results given by Becker et al.,[8] rather than Heller's suggestion.

The molecular structure of the Z-isomer is shown in Fig. 1(b). The torsional angle of C1-C8-C10-C12 is -48.2°, indicating that the π-conjugation is not spread between the furan ring and the succinic anhydride. The succinic anhydride portion is considerably twisted from the planar structure, while the furan ring is retained in the planar structure. The distance between C9 and C12 is 5.339 Å, being quite longer than the distance of E-isomer, 3.443 Å. It seems that the direct cyclization reaction from Z-form to the closed form is improbable thermally as well as photochemically because of the long distance of the reaction sites. Thermal isomerization from the Z-form to the E-form has a high energy barrier because of the C1-C8 double bond. The Z-form is, however, converted to the E-form by the π - π^* excitation followed by rotation through the C1-C8 bond axis in the photoisomerization. The X-ray structure analysis, shown in Fig.1, clearly shows that E-form corresponds to the structure rotated along the C1-C8 axis of Z-form.

References

1) H. G. Heller and S. Oliver, J. Chem. Soc., Perkin Trans. 1, 1981, 197.
2) H. G. Heller and J. R. Langan, J. Chem. Soc., Perkin Trans. 2, 1981, 341.
3) P. J. Darcy, H. G. Heller, P. J. Strydom, and J. Wahittall, J. Chem. Soc., Perkin Trans. 1, 1981, 202.
4) H. G. Heller, IEE Proc., 130, 209 (1983).
5) M. Kaftory, Acta Crystallogr., 40, 1015 (1984).
6) H. Stobbe, Ann., 380, 1 (1911).
7) H. G. Heller and M. Szewczyk, J. Chem. Soc., Perkin Trans. 1, 1974, 1487.
8) C. Lenobbe and R. S. Becker, J. Phys. Chem., 90, 2651 (1986).
9) Y. Yoshioka and M. Irie, in preparation.

(Received August 22, 1988)