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Ab Initio Molecular Orbital Study on Thermal and Photochemical Reactions of 3-Furyl, 3-Pyrryl, and 3-Thienyl Fulgides

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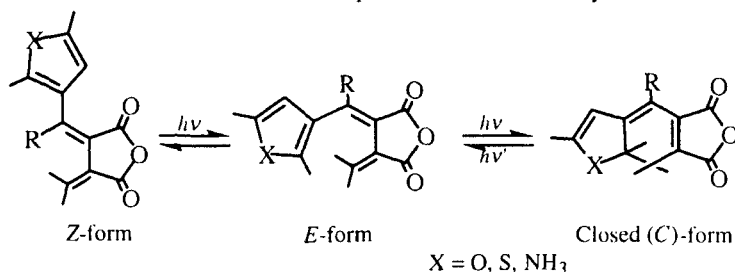
Geometries of 3-Furyl, 3-pyrryl, 3-thienyl fulgides, and substituted 3-furyl fulgides were fully optimized at HF/6-31G and 6-31G* levels. It was found that the *C*-isomers of 3-furyl and 3-thienyl fulgides are more stable than the *E*-isomers, while the *E*- and *C*-isomers are iso-energetic in 3-pyrryl fulgide. The activation energy of thermal ring-closing reaction for 3-furyl fulgide was estimated to be 21 kcal/mol. The electron donating groups enhance the bonding character between atoms to form the single bond in the *C*-isomer.

Keywords: furyl fulgide; pyrryl fulgide; thienyl fulgide; photochromism; photochemical reaction; *ab initio* molecular orbital

INTRODUCTION

3-Furyl, 3-pyrryl, and 3-thienyl fulgides, proposed first by Heller^[1], exhibits characteristics of photochromism making it suitable as typical materials of erasable memory because of its thermal irreversibility^[2]. There are, however, several problems to be solved before it can be applied for industry. The most important problem is its reactivity to the recording and reading light source. The quantum yields of both forward and reverse photoreactions have been improved by introducing bulky substituents such as adamantylidene^[2] or isopropyl^[3]. Although many experimental studies have been performed, there are few theoretical

studies on the molecular structures, the relative stability of isomers, thermal *E-C* isomerization, and the photochemical reactivity.



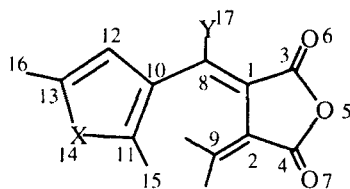
SCHEME 1

Previously, we have theoretically investigated the molecular structures and photochemical reactions of 3-furyl fulgide and its substituted derivatives by *ab initio* molecular orbital (MO) calculations at HF/STO-3G level^[4]. It was found in the photocyclization reaction from the *E*-isomer to the closed (*C*) isomer in which the lowest unoccupied molecular orbital (LUMO) intrinsically has the bonding interaction between the atoms to form the single bond in the *C*-isomer. However, the geometry optimization was limited to the hexatriene and/or cyclohexadiene moieties corresponding to the reaction site and substituents, and basis set was just single-zeta type in the previous work^[4].

In this proceeding, 3-furyl, 3-thienyl, and 3-pyrrolyl fulgides were studied using *ab initio* MO theories with extended basis sets. The *Z*-, *E*-, and *C*-isomers of fulgides were fully optimized at levels of HF/6-31G and HF/6-31G*. Thermal reactions of 3-furyl fulgide and its NH₂-substituted fulgide were investigated to find the transition states and the activation energies in thermal reactions. Substituent effects of photochemical reactions, especially ring-closing reaction from *E*- to *C*-isomer, were also investigated from the population of reaction site.

CALCULATIONAL DETAILS

The heavy atoms in fulgide molecules are numbered as follows,



(X, Y)

Y = -CH₃, -CH₂CH₃, -CH(CH₃)₂, -NH₂, -OH, -NO₂, -CN

SCHEME 2

We employed the abbreviation such as (X,Y) to easily indicate all fulgides investigated here. For example, (O,-CH₃) and (NCH₃,-CH₃) means respectively the typical 3-furyl and 3-pyrrolyl fulgides proposed by Heller^[1]. Yokoyama and Kurita showed that the substitution of bulky functional groups such as ethyl and isopropyl to the position of Y17 increases the quantum yield of photocyclization from the *E*- to *C*-isomer^[3]. It is interesting to investigate the substitution effect introduced at Y17 position for thermal stability, thermal reaction, and photoreaction. We employed -CH₂CH₃ and -CH(CH₃)₂ as bulky alkyl groups, -NH₂ and -OH as electron donating groups, and -NO₂ and -CN as electron accepting groups.

The spin-restricted Hartree-Fock (RHF) method was employed for full geometry optimization of three typical fulgides, (O, -CH₃), (NCH₃, -CH₃), and (S, -CH₃), using the program package of Gaussian 98^[5] with 6-31G and 6-31G* basis sets. The geometries of substituted 3-furyl fulgides, (O, -CH₂CH₃), (O, -CH(CH₃)₂), (O, -NH₂), (O, -OH), (O, -NO₂), and (O, -CN) were also fully optimized at RHF/6-31G* level.

The RHF method is not suitable for finding the transition state of the thermal pericyclic reaction because of instability of the RHF solution. The singlet unrestricted Hartree-Fock (UHF) was employed to find the transition state of thermal reaction between *E*- and *C*-isomers of (O, -CH₃) and (O, -NH₂) using 6-31G* basis set.

GEOMETRIES AND RELATIVE STABILITIES

The optimized geometries are briefly summarized. All geometrical

parameters are open from one of authors, Y.Y.

- 1) Both *E*- and *Z*-isomers have twisted structures between the heteroring and the succinic anhydride moieties. The twisted angles C11-C10-C8-C1 of (O,-CH₃) are given by -55.7° and -54.3° for *E*- and *Z*-isomers at HF/6-31G* level, respectively, being consistent with -41.9° and -48.2° examined by X-ray analysis^[6]. They are also, respectively, -54.8° and -51.4° for *E*- and *Z*-isomers of (NCH₃,-CH₃), and -59.3° and -64.2° for (S,-CH₃).
- 2) The *C*-isomers of (O,-CH₃), (NCH₃,-CH₃), and (S,-CH₃) have planar structures with extended π -resonance, being consistent with absorption band appeared in the visible region.

TABLE I Relative stability (kcal/mol) of *Z*-, *E*-, and *C*-isomers of three typical fulgides.

| Method | <i>Z</i> -isomer | <i>E</i> -isomer | <i>C</i> -isomer |
|--|------------------|-------------------|------------------|
| (O,-CH ₃) | | | |
| HF/MNDO//HF/MNDO ^{a)} | -0.8 | 0.0 | 15.6 |
| HF/STO-3G//HF/STO-3G ^{b)} | 0.2 | 0.0 | -30.2 |
| HF/4-31G//HF/STO-3G ^{b)} | 1.2 | 0.0 | -8.7 |
| HF/6-31G//HF/6-31G | 0.5 | 0.0 ^{c)} | -6.1 |
| HF/6-31G*//HF/6-31G | 0.1 | 0.0 ^{d)} | -10.3 |
| HF/6-31G*//HF6-31G* | 0.4 | 0.0 ^{e)} | -10.0 |
| (-NCH ₃ ,-CH ₃) | | | |
| HF/6-31G//HF/6-31G | 0.2 | 0.0 ^{f)} | 8.4 |
| HF/6-31G*//HF/6-31G | 0.0 | 0.0 ^{g)} | 2.6 |
| HF/6-31G*//HF6-31G* | 0.3 | 0.0 ^{h)} | 1.7 |
| (S,-CH ₃) | | | |
| HF/6-31G//HF/6-31G | 1.4 | 0.0 ⁱ⁾ | -5.0 |
| HF/6-31G*//HF/6-31G | 0.8 | 0.0 ^{j)} | -6.4 |
| HF/6-31G*//HF6-31G* | 0.8 | 0.0 ^{k)} | -6.1 |

3) Ref. [4b]. b) Ref. [4d]. Total energies are respective c) -876.38344 au, d) -876.77687 au, e) -876.78265 au, f) -895.59117 au, g) -895.98515 au, h) -895.98947 au, i) -1199.03779 au, j) -1199.42891 au, k) -1199.43588 au.

Table I shows the relative stability of *Z*-, *E*-, and *C*-isomers of typical fulgides, (O,-CH₃), (NCH₃,-CH₃), and (S,-CH₃). For all fulgides, the *Z*-isomers are isoenergetic states to the *E*-isomers. The relative stability between *E*- and *C*-isomers is largely dependent on the calculation method and basis sets used. The double zeta with polarization indicates that the *C*-isomers of (O,-CH₃) and (S,-CH₃) are more stable by 10 and 6 kcal/mol, respectively, while the *C*-isomer of (NCH₃,-CH₃) is slightly higher than the *E*-isomer. It should be considered from Table I that the polarization function has to be taken into account for describing the stability and the electronic structures of the fulgide molecules including the heteroring.

Table II summarizes the relative stability between three isomers of substituted 3-furyl fulgides. The alkyl substituents do not change the relative stability among three isomers and the electron accepting groups induce the stabilization of the *C*-isomer compared with alkyl group. It is, therefore, expected that the *C*-isomer does not occur the ring opening by their substituents. On the other hand, the electron donating groups make the *C*-isomer unstable, compared with the *E*-isomer.

TABLE II Relative stability (kcal/mol) of three isomers of substituted 3-furyl fulgides, (O, Y), optimized at HF/6-31G* level.

| | <i>Z</i> -isomer | <i>E</i> -isomer | <i>C</i> -isomer |
|--------------------------------------|------------------|-------------------|------------------|
| Y=-CH ₃ | 0.4 | 0.0 ^{a)} | -10.0 |
| Y=-CH ₂ CH ₃ | 1.9 | 0.0 ^{b)} | -9.9 |
| Y=-CH(CH ₃) ₂ | 2.0 | 0.0 ^{c)} | -9.9 |
| Y=-NH ₂ | 3.8 | 0.0 ^{d)} | 3.7 |
| Y=-OH | 4.5 | 0.0 ^{e)} | 3.5 |
| Y=-NO ₂ | -2.0 | 0.0 ^{f)} | -15.5 |
| Y=-CN | -3.2 | 0.0 ^{g)} | -15.4 |

Total energies are respectively a) -876.78265 au, b) -915.81688 au, c) -954.84625 au, d) -892.79158 au, e) -912.61792 au, f) -1041.19962 au, and g) -929.46906 au.

THERMAL REACTIONS OF 3-FURYL FULGIDES

Table III shows the activation energies of the thermal *E*-*C* isomerization. The transition states correspond to the disrotatory mode of 6π electrocyclization proposed by Woodward and Hoffmann^[7]. In the case of (O,-CH₃), the activation energy of the reaction from *C*- to *E*-isomer is quite high in energy, 31.4 kcal/mol, showing that the colored *C*-isomer does not proceed thermally to the *E*-isomer. The activation energy of the bleaching reaction for (O,-NH₂) is 25.5 kcal/mol, being smaller than that for (O,-CH₃). However, for the disrotatory cyclization from *E*- to *C*-isomer, the activation energies of 21.4 and 29.2 kcal/mol for (O,-CH₃) and (O,-NH₂) are quite small, compared with 37 kcal/mol for *cZc*-hexatriene^[8], indicating that addition of heteroring and succinic anhydride to hexatriene backbone decreases the activation energy of 6π electrocyclization.

TABLE III C9-C11 distances (Å) and relative energies (kcal/mol) for thermal reaction between *E*- and *C*-isomers at HF/6-31G* level.

| | (O, -CH ₃) | | (O, -NH ₂) | |
|----------------|--------------------------|-------------------------|--------------------------|-------------------------|
| | <i>R</i> ₉₋₁₁ | <i>E</i> _{rel} | <i>R</i> ₉₋₁₁ | <i>E</i> _{rel} |
| <i>E</i> -form | 3.623 | 0.0 | 3.669 | 0.0 |
| TS | 2.243 | 21.4 | 2.214 | 29.2 |
| <i>C</i> -form | 1.549 | -10.0 | 1.552 | 3.7 |

a) TS means the transition state of *E*-*Z* isomerization.

The distances, C9-C11, of (O,-CH₃) and (O,-NH₂) are, respectively, given by 2.243 Å and 2.214 Å as shown in Table III. It is interesting that these are comparable with 2.292 Å of cyclization of *cZc*-hexatriene^[8]. This indicates that the geometry of transition state of thermal electrocyclization for the hexatriene moiety is not relatively changed by inclusion of substituents such as heteroring and succinic anhydride moieties.

SUBSTITUENT EFFECTS OF PHOTOCHEMICAL REACTIONS OF 3-FURYL FULGIDES

We demonstrated in previous work^[4] that the LUMO of the *E*-isomer play an important role in the photocyclization reaction from *E*- to *C*-isomer. The LUMO has through-space bonding interaction between atoms of C9 and C11 to form the single bond in the *C*-isomer.

Table IV shows the electron population between C9 and C11 in the LUMO of *E*-isomer. The electron donating groups, compared with the alkyl groups, increase the bonding interaction between C9 and C11 due to the electronic effects such as increasing the charge density of the reaction site C11. This indicates that the quantum yield of the photocyclization reaction is expected to be increased. On the other hand, the electron accepting groups decrease the bonding interaction, showing that the quantum yield will be decreased.

TABLE IV C9-C11 distances (Å), atomic charge densities on C9 and C11, electron population between C9 and C11 in the LUMO of the *E*-isomer of the substituted 3-furyl fulgide.

| (O,Y) | R_{9-11} | ρ_9 | ρ_{11} | ρ_{9-11} |
|-------------------------------------|------------|----------|-------------|---------------|
| Y=CH ₃ | 3.623 | 0.4142 | 0.1016 | 0.004086 |
| Y=CH ₂ CH ₃ | 3.630 | 0.4001 | 0.1127 | 0.003921 |
| Y=CH(CH ₃) ₂ | 3.623 | 0.4225 | 0.0893 | 0.002900 |
| Y=NH ₂ | 3.669 | 0.3787 | 0.1708 | 0.005143 |
| Y=OH | 3.689 | 0.4031 | 0.1692 | 0.004043 |
| Y=NO ₂ | 3.757 | 0.4037 | 0.1089 | 0.002572 |
| Y=CN | 3.660 | 0.3069 | 0.0800 | 0.002708 |

SUMMARY

The molecular structures of three isomers of 3-furyl, 3-pyrrolyl, 3-thienyl fulgides, and substituted 3-furyl fulgides were determined by *ab initio* molecular orbital theory. The thermal and photochemical reactions were also investigated at HF level. The *C*-isomers of 3-furyl and 3-thienyl fulgides are more stable by 10 and 6 kcal/mol than the *E*-isomers, respectively, while the *E*- and *C*-isomers are isoenergetic in 3-pyrrolyl fulgide. The electron donating groups in 3-furyl fulgide alter stability between *E*- and *C*-isomers. The activation energy of thermal ring

closing reaction for 3-furyl fulgide was estimated to be 21 kcal/mol. In the excited state of the *E*-isomer, the electron donating groups enhance the bonding character between atoms to form the single bond in the *C*-isomer.

Acknowledgments

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