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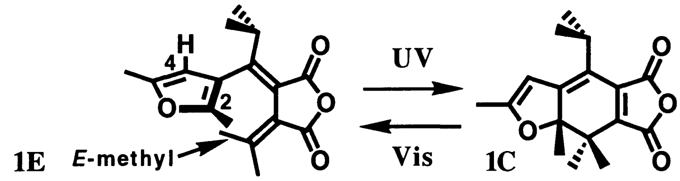
Helical Chirality and Enantiotopomerization Process of a Photochromic Furylfulgide

Yayoi YOKOYAMA,* Takeshi IWAI,† Yasushi YOKOYAMA,*,† and Yukio KURITA†
Faculty of Home Economics, Tokyo Kasei Gakuin University, 2600, Aihara-cho, Machida, 194-02
†Department of Materials Chemistry, Faculty of Engineering, Yokohama National University,
156, Tokiwadai, Hodogaya-ku, Yokohama 240

A photochromic furylfulgide, (*E*)-2-[1-(2,5-dimethyl-3-furyl)-2-methylpropylidene]-3-isopropylidenesuccinic anhydride, was shown to be chiral. Its enantiotopomerization process was observed by variable temperature ^{1}H NMR measurement, and $\Delta H^{\neq}$(obs) was 52.9 ± 8.1 kJ mol^{-1}. AM1 calculation showed $\Delta H^{\neq}$(calc) to be 51.5 kJ mol^{-1}.

Fulgides such as **1** are the representative thermally irreversible organic photochromic compounds.1) Although their overcrowded structural feature has been well documented, literatures concerning their chirality are rare.2) We here report that the fulgide **1E** is intrinsically chiral, and the enantiotopomerization occurs easily.

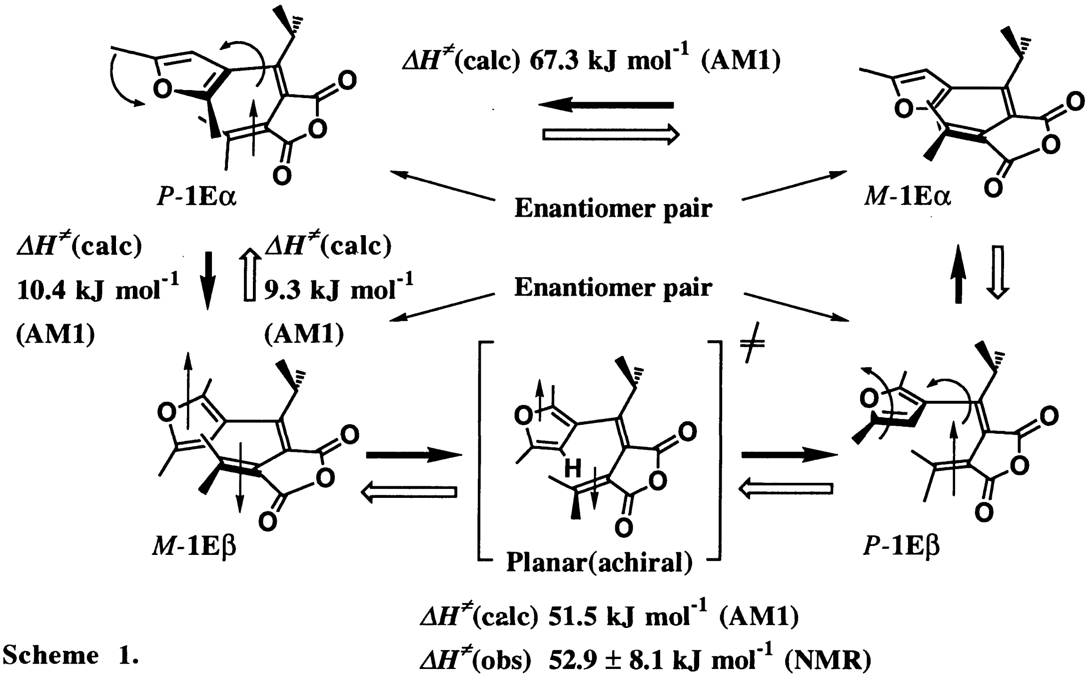


The chirality of the fulgide **1E** was recognized by the appearance of the signals of two methyl groups of the isopropyl group in 270 MHz ^{1}H NMR spectra measured in $CDCl_3$. At -20 °C, the two methyl groups appeared as two sets of doublets (δ 0.88 (J = 6.93 Hz) and 1.33 (J = 6.93 Hz), each 3H), while they became broad peaks when the measurement temperature raised. Finally, they coalesced at 52 °C. The fact that two methyl groups of the isopropyl group appeared at the different chemical shifts means that this molecule is chiral, and the broadening of the signals and coalescence mean that the enantiotopomerization does occur. With 90 MHz ^{1}H NMR apparatus, they coalesced at 35.5 °C. From these results, $\Delta G^{\neq}$(52 °C) and $\Delta G^{\neq}$(35.5 °C) were calculated with Eyring equation to be 64.7 ± 0.2 kJ mol^{-1} 3) and 64.1 ± 0.2 kJ mol^{-1}, respectively. Therefore $\Delta H^{\neq}$(obs) of enantiotopomerization is 52.9 ± 8.1 kJ mol^{-1} and $\Delta S^{\neq}$(obs) -36.5 ± 24.2 J K^{-1} mol^{-1}.5)

The enantiotopomerization mechanism was then considered. As the furan plane cannot be in the crowded plane consisting of the acid anhydride with two double bonds, the furan ring should be twisted as **1Eα** (the two carbon atoms forming a C-C bond when irradiated with UV light are close) or **1Eβ** (the two carbon atoms are remote). As both conformations are helically chiral, they have *P* and *M* enantiomers as shown in Scheme 1.

The enantiotopomerization observed by ^{1}H NMR could occur when the *E*-methyl group of the isopropylidene group passes by either the 2-methyl group or the 4-H of the furan group (as between *P*-**1Eα** and *M*-**1Eα** or between *M*-**1Eβ** and *P*-**1Eβ**, respectively). On the other hand, diastereotopomeric isomerization from **1Eα** to **1Eβ** and from **1Eβ** to **1Eα** *via* the "over the hill" motion of the furan around the *E*-methyl of the isopropylidene group could also occur.

The enthalpy barrier of enantiotopomerization between *P*-**1Eα** and *M*-**1Eα** was calculated to be 67.3 kJ mol^{-1} by AM1 semiempirical molecular orbitals calculation.[5] On the other hand, the enthalpy barrier between *M*-**1Eβ** and *P*-**1Eβ** was calculated to be 51.5 kJ mol^{-1}, which is in good agreement with the value obtained from ^1H NMR. Since the enthalpy barrier of diastereotopomerization from *P*- and *M*-**1Eα** to *M*- and *P*-**1Eβ** and from *M*- and *P*-**1Eβ** to *P*- and *M*-**1Eα** were calculated to be 10.4 and 9.3 kJ mol^{-1}, respectively, the interconversions between them occur smoothly at room temperature. This means that the enantiotopomerization of **1E** occurs mostly between the two enantiomers of **1Eβ** which can easily diastereotopomerize to **1Eα**.



Scheme 1.

That fulgides exist as racemates is quite important. If optically active fulgides would be synthesized, it should show interesting photochromic behaviors.[6] Efforts to obtain optically active, non-racemizable fulgide derivatives are now under way in our laboratory.

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