Study on the Conformation of an Isopropyl-Substituted Furylfulgide. Photochromic Coloring Reaction and Thermal Racemization

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The conformations of the *E*-forms of photochromic furylfulgides with a methyl substituent (**1E**) and an isopropyl substituent (**2E**) were investigated by X-ray crystallographic analyses, NMR measurements, and molecular orbital (MO) calculations in relation to the large quantum yield of the coloring reaction of **2E** upon the irradiation of UV light. The conformations of **1E** and **2E** obtained by X-ray crystallographic analyses are the photocyclization-possible ones ($\mathbf{E}_\alpha$), in which the distances of the bond-forming carbon atoms of **1E** and **2E** are essentially the same. NOESY of ^{1}H NMR measurements of **1E** and **2E** showed that they take both the $\mathbf{E}_\alpha$ and cyclization-impossible $\mathbf{E}_\beta$ conformations in solution. Although MO calculations of **2E** proved that the population of $\mathbf{2E}_\alpha$ is dominant when the entropy contributions of the rotation of substituents are considered, the large difference in the quantum yields was not fully elucidated. The difference may have come from a difference in the nature of the excited states of **1E** and **2E**, which is evidenced by the large difference in the molar absorption coefficient (**1E**: 6700, **2E**: 4250 mol^{-1} dm^3 cm^{-1} in toluene).

The thermodynamic parameters of the enantiotopomerization process of **2E** were determined by variable-temperature ^{1}H NMR measurements. The mechanism of enantiotopomerization was specified by MO calculations.

Fulgides are one of the representative thermally irreversible photochromic compounds.[1] The change in the absorption spectra between the colorless (or slightly yellow) and deeply colored (yellow, orange, red, purple, blue, or green) species upon the irradiation of UV light in solution is drastic. Although the application of fulgides to rewritable optical memory was first intended,[2—4] other utilizations based on their structural changes by the photochromic reactions have also been considered.[5—9] In any aspects concerning the application of fulgides to the photoswitchable functional materials, large quantum yields of photochromic transformations should be welcomed.

The photochromism of furylfulgides involves photoinduced electrocyclic transformation between the *E*-(colorless) and *C*-forms (red) as well as *E*–*Z* isomerization.[10] We have recently showed that the steric bulkiness of alkyl substituents on the furylmethylene moiety of furylfulgides strongly influence the coloring as well as the *E*-to-*Z* isomerization quantum yields.[11,12] Although the coloring and *E*-to-*Z* isomerization quantum yields of the furylfulgide **1E**, with a methyl group on the furylmethylene group, are 0.19 and 0.13, respectively, those of the furylfulgide **2E**, with an isopropyl group, are 0.62 and 0, respectively, in chloroform (Chart 1). Since the proportion of deexcitation of **1E** is there-

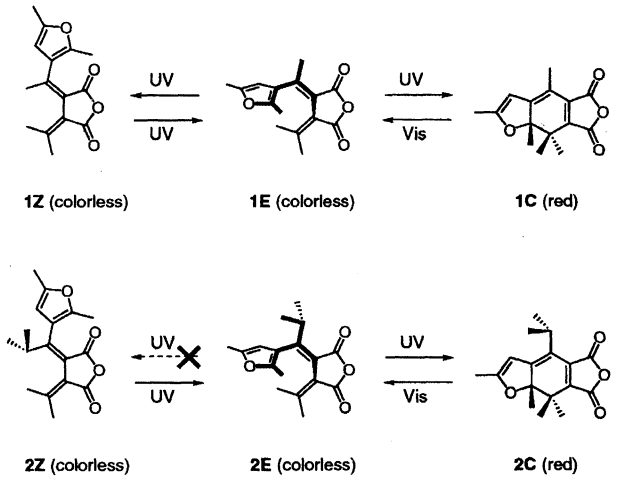

Chart 1.

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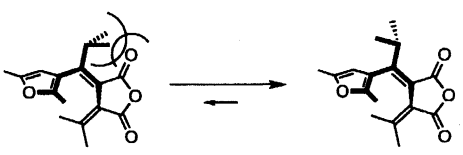
fore 0.68 (subtract 0.19 and 0.13 from unity) and that of **2E** is 0.38 (subtract 0.62 from unity), the difference in the coloring quantum yield between **1E** and **2E** is not only that the portion of *E*-to-*Z* isomerization of the excited-state molecules of **1E** goes over to the cyclization for **2E**, but also that the cyclization itself becomes easier for **2E** upon UV-light irradiation. Since the electronic properties of **1** and **2** may not greatly differ, the difference in the coloring quantum yield arises due to the steric reasons. In 1990, Ilge et al. reported on the relationship between the bulkiness of the alkyl substituents and the cyclization and *E*-to-*Z* isomerization quantum yields.[13] They assumed that an increase in the bulkiness of the alkyl group would cause a torsion of the isopropylidene double bond, and that the torsion (up to 40°) would cause a change in the electronic state of fulgides. However, it is not obvious how the bulkiness of the alkyl group can induce a torsion of the isopropylidene double bond, which is located far from the alkyl group.

When we observed a large quantum yield of coloring and no *E*-to-*Z* isomerization for **2E** upon irradiation of 366-nm light, we hypothesized that there were two stable ground-state conformations ($\mathbf{E}_\alpha$ and $\mathbf{E}_\beta$) for the *E*-form of a furylfulgide (Chart 2), where $\mathbf{E}_\alpha$ was able to cyclize to the colored form **C**, and $\mathbf{E}_\beta$ was not able to cyclize.[11] If the cyclization of $\mathbf{E}_\beta$ would occur, it should generate an *E,Z*-1,3-cyclohexadiene unit that is highly strained. As for **2E**, in order to avoid a severe allylic 1,3-strain[14,15] between the methyl groups (Me(20) and Me(21)) of the isopropyl moiety and the proximate carbonyl oxygen (O(6)), the tertiary hydrogen of the isopropyl (H(17)) might be forced to face the carbonyl oxygen (Chart 3). This was evidenced by ^{1}H NMR, that while the chemical shift of the methine proton of **2Z** was δ = 2.84, that of **2E** was δ = 4.29 in $CDCl_3$.[12] This difference can be rationalized by saying that the methine proton of **2E** suffers from a deshielding effect of the carbonyl group. Consequently, two methyl groups of the isopropyl group of **2E** come closer to the furan ring.

In the following sections we describe our efforts to clarify the origin of the large coloring quantum yield of **2E** by means of X-ray crystallography, NMR measurements, and molecular-orbital calculations, as well as UV-vis absorption spectra. The basic idea was, according to the NEER (Non Equilibration of Excited Rotamers) principle,[16] to prove that the ratio of the $\mathbf{E}_\alpha$ conformation is larger for **2E** than for **1E**.

$\mathbf{E}_\alpha$ $\mathbf{E}_\beta$

Chart 2.



2E

Chart 3.

As a different story, *E*-forms of fulgides have been supposed to exist as enantiotopomeric mixtures of helical chirality due to the spiral array of the two methylene substituents on the succinic anhydride ring on the basis of X-ray crystallographic analyses of *E*-, *Z*-, and *C*-forms of a thienyl fulgide reported by Kaftory.[17] We would like to describe the enantiotopomerization process[18] of an isopropyl-substituted furylfulgide based on NMR measurements and molecular-orbital calculations.

Results and Discussion

Crystal Structure of Fulgides 1E and 2E. A number of determinations of fulgide structures by X-ray crystallographic analyses have been reported to date.[17,19—27] Among them, Kaftory's report[17] is notable because it is the first example of a determination of the structure of the colored form.[27] His work unequivocally confirmed the mechanism of the cyclization reaction of fulgides to be 6π electrocyclization. The crystal structures of **1E** and **1Z** were reported by Yoshioka et al. in 1989.[20] We determined the crystal structure of **2E** by X-ray diffraction. In addition, we determined the structure of **1E** again, and confirmed that the structure of **2E** is essentially the same as that of **1E**.

From Figs. 1a and 1b, we can see that both **1E** and **2E** take the $\mathbf{E}_\alpha$ conformation in the crystals. Since the distances between the carbon atoms to form a single bond by UV-light irradiation (C(9) and C(12)) for **1E** (0.3445(4) nm) and **2E** (0.3441(4) nm) are almost the same, the difference in the coloring quantum yield could not be explained based on this result.

It should be emphasized that, since we had assumed from the ^{1}H NMR data of **2E** that the methine hydrogen of the isopropyl group of **2E** (H(11)) faces the proximate carbonyl oxygen (O(6)), the two methyl groups are pushed away toward the furan ring.

As shown in Figs. 1a and 1b, each molecule takes a helical $\mathbf{E}_\alpha$ conformation in crystals. Due to the centrosymmetry of the crystals ($P2_1/n$ for **1E** and $P2_1/c$ for **2E**), **1E** and **2E** exist as racemic mixtures of the helical $\mathbf{E}_\alpha$ conformations in crystals.[28]

Thus, the furylfulgides take the $\mathbf{E}_\alpha$ conformation in their crystalline states. However, there must be another conformation, $\mathbf{E}_\beta$. We next consider the conformations of fulgides **1E** and **2E** in solution on the basis of an observation obtained by NMR measurements.

NMR Study of 1E and 2E. Although the assignments of the signals of ^{1}H and ^{13}C NMR for **1E** have already been published,[29,30] those for **2E** have not. We assigned the ^{13}C and ^{1}H NMR signals of **2E** with the 2D-INADEQUATE method and C-H COSY, according to the same method used for **1E**.[30]

We then tried the 2D-NOESY method (Fig. 2a and 2b). For **1E**, the nuclear Overhauser effects (NOEs) ascribed to $\mathbf{1E}_\alpha$ were observed between H(11) and Me(17) (abbreviated

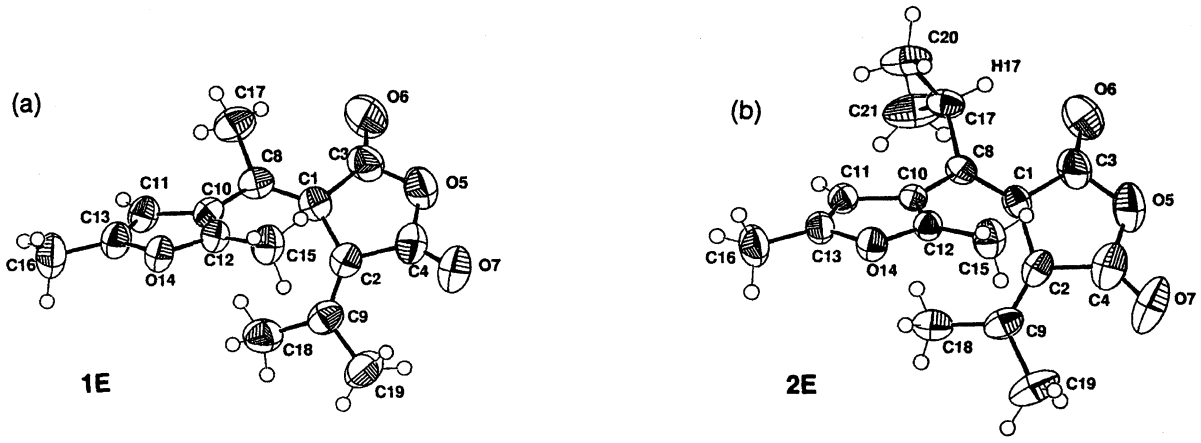


Fig. 1. ORTEP diagram. (a) **1E**. (b) **2E**.

as H(11)/Me(17) hereafter) and Me(15)/Me(18), whereas those ascribed to $\mathbf{1E}_\beta$ were observed between Me(15)/Me(17) and Me(16)/Me(18). For **2E**, the NOEs ascribed to $\mathbf{2E}_\alpha$ were observed between H(11)/Me(20), H(11)/Me(21), Me(15)/Me(18), and Me(15)/Me(19), whereas those ascribed to $\mathbf{2E}_\beta$ were observed between Me(15)/Me(20), Me(15)/Me(21), and Me(16)/Me(18).

Thus, the NOE studies confirmed that **1E** and **2E** take both the $\mathbf{E}_\alpha$ and $\mathbf{E}_\beta$ conformations in $CDCl_3$ at room temperature. Since quantitative assumption concerning the conformer ratio is not possible for NOE studies, the difference in $[\mathbf{E}_\alpha]/[\mathbf{E}]$ between **1E** and **2E** was not determined. We therefore next tried to evaluate the difference by molecular orbital calculations.

AM1 Molecular-Orbital Calculations. Starting from the conformation obtained from the X-ray crystallographic analysis, we obtained the locally most stable conformation for **1E** and **2E**, corresponding to $\mathbf{1E}_\alpha$ and $\mathbf{2E}_\alpha$, respectively, by AM1 semiempirical molecular-orbital calculation methods (Fig. 3).[31] The distances between the bond-forming carbon atoms (C(9) and C(12)) were calculated to be 0.356 nm and 0.357 nm for **1E** and **2E**, respectively. Like the results from X-ray crystallographic analyses (0.3445(4) nm for **1E** and 0.3441(4) nm for **2E**), little difference was shown again, although each distance was longer than that obtained from X-ray analyses. The calculated structures are quite similar to those of the X-ray structures as a whole. The slight differences might have resulted from the neglecting the intermolecular interactions that should exist in the crystals. For example, the calculated dihedral angles of C(3)–C(1)–C(2)–C(9) and C(1)–C(8)–C(10)–C(11) of **2E** are −154.92° and −121.89°, respectively, whereas those of X-ray analysis are −149.1(2)° and −137.2(3)°, respectively.

Next, the other stable conformation, which we had designated as $\mathbf{E}_\beta$, was searched for. Starting from the conformations after the 180°-rotation of the furan-alkylidene single bond (C(8)–C(10)) of $\mathbf{1E}_\alpha$ and $\mathbf{2E}_\alpha$, we obtained locally stable conformations, $\mathbf{1E}_\beta$ and $\mathbf{2E}_\beta$ (Fig. 4). The values of H_f as well as ΔH_f (with regard to $\mathbf{E}_\alpha$ conformations) of the stable conformations are listed in Table 1. From these data, we can obtain the population ratios of the cyclizable conformers, $[\mathbf{1E}_\alpha]/[\mathbf{1E}]$ and $[\mathbf{2E}_\alpha]/[\mathbf{2E}]$, at some designated temperature, on the basis of the assumptions that: (i) $\mathbf{E}_\alpha$ and $\mathbf{E}_\beta$ are thermally equilibrated, and therefore obey Maxwell–Boltzmann's distribution; and (ii) the contributions of entropy are the same for $\mathbf{E}_\alpha$ and $\mathbf{E}_\beta$. The ratio $[\mathbf{1E}_\alpha]/[\mathbf{1E}]$ at 25 °C is 0.601, and $[\mathbf{2E}_\alpha]/[\mathbf{2E}]$ is 0.606, suggesting that there would be no population difference between $\mathbf{1E}_\alpha$ and $\mathbf{2E}_\alpha$ with regard to the cyclizable conformations of **1E** and **2E** with the assumptions described above.

Table 1. Heat-of-formation values of the local minimum conformers of **1E** and **2E**, and heat-of-formation differences of them with regard to the corresponding $\mathbf{E}_\alpha$ conformers.

	H_f/kJ mol^{-1}	ΔH_f/kJ mol^{-1}
$\mathbf{1E}_\alpha$	−399.18	0
$\mathbf{1E}_\beta$	−398.17	1.01
$\mathbf{2E}_\alpha$	−429.10	0
$\mathbf{2E}_\beta$	−428.03	1.07

Further insights, i.e. the entropy terms concerning the curvature of the potential surfaces of the rotation of the furan-alkylidene single bond (C(8)–C(10)) for both conformations of **1E** and **2E**, and that of rotation of the isopropyl group (C(8)–C(17)) for $\mathbf{2E}_\alpha$ and $\mathbf{2E}_\beta$, are required.

The shapes of the potential-energy surfaces of **1E** and **2E** with regard to the rotation of furan, presented by the dihedral angle of C(1)–C(8)–C(10)–C(11), are shown in Figs. 4a and 4b. From these figures it is apparent that: (i) the curvature around $\mathbf{1E}_\alpha$ is larger than that around $\mathbf{1E}_\beta$; and (ii) the curvature around $\mathbf{2E}_\alpha$ is almost the same as that around $\mathbf{2E}_\beta$. Therefore, while the distribution of **1E** molecules between $\mathbf{1E}_\alpha$ and $\mathbf{1E}_\beta$ is slightly biased in favor of $\mathbf{1E}_\beta$, when the curvature of the potential energy surfaces are taken into consideration that of **2E** molecules between $\mathbf{2E}_\alpha$ and $\mathbf{2E}_\beta$ must not change largely. Further and quantitative treatments to obtain the vibrational energy levels and the population distribution for them, however, were not carried out.

Another freedom of the intramolecular motion of **2E**, which is lacking for **1E**, is the rotation of the isopropyl group.

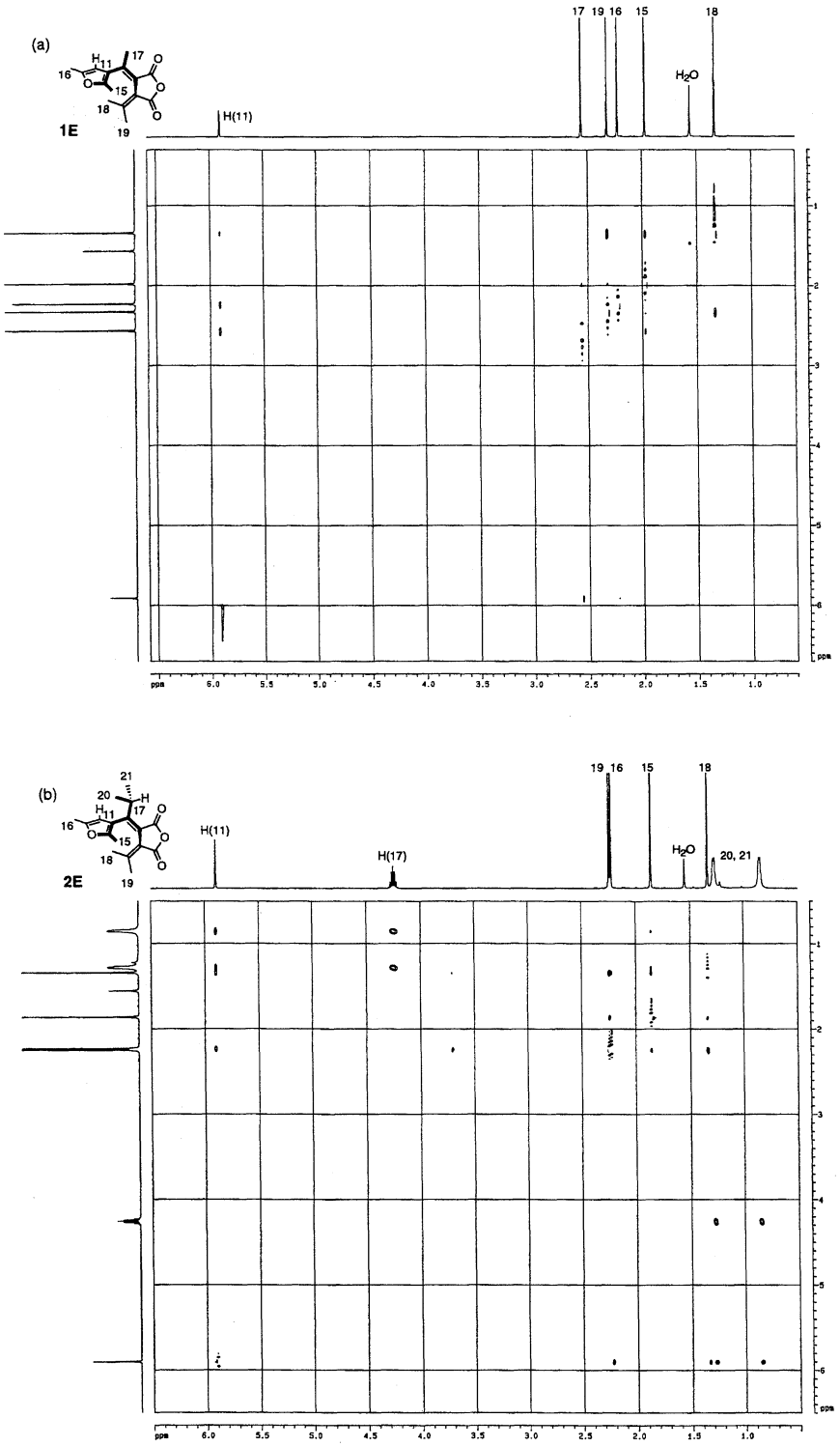


Fig. 2. NOESY spectrum in $CDCl_3$ (500 MHz). (a) **1E**. (b) **2E**.

We next inspected the shapes of their potential-energy surfaces. The shapes of the potential surfaces of $\mathbf{2E}_\alpha$ and $\mathbf{2E}_\beta$ with regard to the rotation of the isopropyl group, presented by the dihedral angle of C(20)–C(17)–C(8)–C(1), are shown in Fig. 5. Since Me(15) is obviously compressing Me(20) and Me(21) in $\mathbf{2E}_\beta$, the rotation of the isopropyl group must be much more constrained in $\mathbf{2E}_\beta$ than in $\mathbf{2E}_\alpha$ (this compression is not expected in $\mathbf{1E}_\beta$). As shown in Fig. 5, the absolute value, itself, of the minimum of $\mathbf{2E}_\alpha$ is lower than that of $\mathbf{2E}_\beta$. Furthermore, the total shape of the well of $\mathbf{2E}_\alpha$ is flatter than that of $\mathbf{2E}_\beta$. Therefore, the difference in the total free energy between $\mathbf{2E}_\alpha$ and $\mathbf{2E}_\beta$ is larger than the value without taking the rotation of isopropyl group into consideration.

It should be noted that the arrangement of the carbon atoms (C(1)–C(8)–C(10)–C(11)) of $\mathbf{1E}_\alpha$ ($-133.79°$) is flatter than

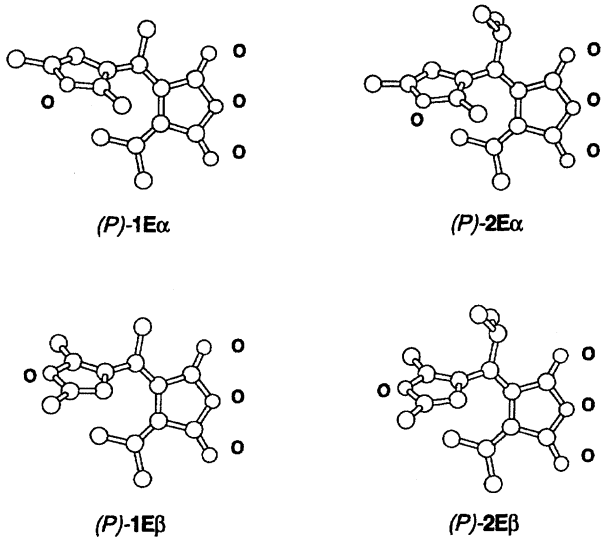
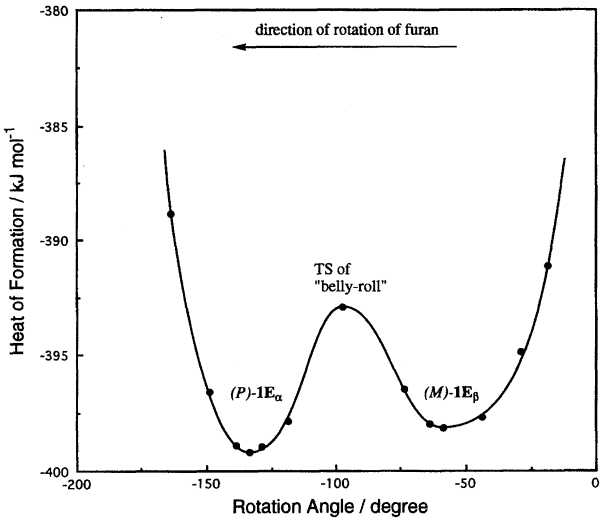


Fig. 3. Conformations of **1E** and **2E** possessing local minimum H_f values.



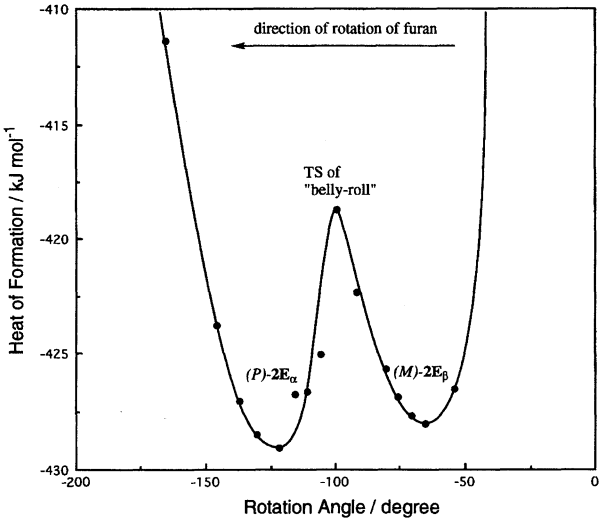


Fig. 4. Plots of H_f vs. rotation of dihedral angle of C(1)–C(8)–C(10)–C(11). (a) **1E**. (b) **2E**.

that of $\mathbf{2E}_\alpha$ (−121.89°). This means that the overlapping of the atomic orbitals between C(9) and C(12) in $\mathbf{2E}_\alpha$ is larger than that in $\mathbf{1E}_\alpha$, in that the flatter conformation makes the orbitals to lie closer to parallel. This may also contribute to the larger cyclization quantum yield of **2E** than that of **1E**.

The entropy terms therefore play an important role to determine the population of the conformational isomers in **2E**. Although these data are qualitative, the tendency of largeness of the cyclization quantum yield of **2E** was reproduced. However, we were not satisfied with the results mentioned above. The large difference in the quantum yield of photocyclization did not seem to be fully elucidated.

UV-vis Spectroscopic Properties of 1E and 2E. We have realized that the molar absorption coefficient of **2E** (4250 $mol^{-1}\,dm^3\,cm^{-1}$ at λ_{max} (342 nm) in toluene, 4080 $mol^{-1}\,dm^3\,cm^{-1}$ at λ_{max} (347 nm) in chloroform) is substantially smaller than that of **1E** (6700 $mol^{-1}\,dm^3\,cm^{-1}$ at λ_{max} (343 nm) in toluene, 6780 $mol^{-1}\,dm^3\,cm^{-1}$ at λ_{max} (347 nm) in chloroform), although the absorption maximum wavelengths are practically the same. That **2E** molecules do not aggregate in these solvents was confirmed by measuring the absorption spectra with different concentrations. Since the electronic characters of both fulgides must not differ greatly, the difference should be caused by sterical reasons. In other words, the isopropyl group might have worked to reduce the transition moment of the $\pi\pi^*$ electronic excitation, although the reasons are not known. Furthermore, if the structure of the excited state of furylfulgides takes the twisted intramolecular charge-transfer (TICT) type structure by rotating the C(1)–C(8) double bond from the Franck–Condon state,[32,33] the isopropyl substituent of **2E** should come close to the isopropylidene group, and should suffer a strong steric repulsion. This repulsion prohibited the generation of **2Z**, and the difference of the nature of the excited state exemplified by the small ε may be the large coloring quantum yield of **2E**. Since a quantitative elucidation of the nature of the excited state is quite difficult today, any exploration to uncover the reasons for the large coloring quantum yield of **2E** must be postponed until a molecular-orbital calculation method which can give the reliable information about the nature of the excited states becomes available.

Thermal Enantiotopomerization Process of Furylfulgide 2E. During the course of our study described above, we realized that the two methyl groups of the isopropyl group of **2E** appeared as a set of two distorted doublets on the ^1H NMR spectrum at room temperature in $CDCl_3$ (Fig. 6). At −20 °C, they appeared as two sets of doublets (δ = 0.882, 3H, d, J = 6.93 Hz and δ = 1.330, 3H, d, J = 6.93 Hz). Together with the observation that a single crystal of **2E** comprises an equimolar amount of enantiotopomeric isomers, the phenomenon observed in the NMR study strongly suggests the occurrence of enantiotopomerization. We therefore carried out a variable-temperature NMR study. With a

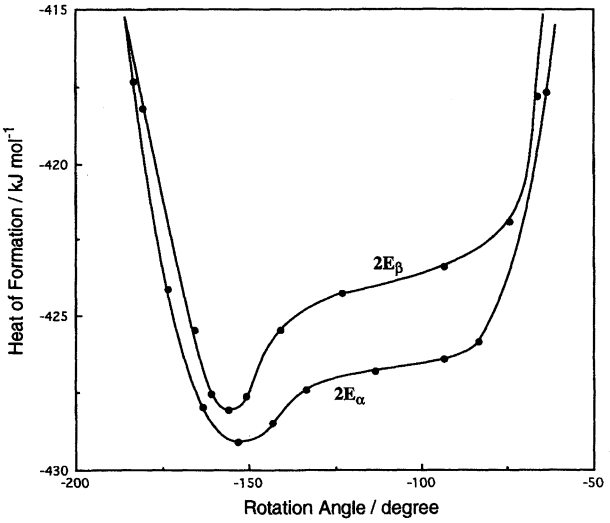


Fig. 5. Plots of H_f vs. rotation of dihedral angle of C(20)–C(17)–C(8)–C(1) of **2E**$_\alpha$ and **2E**$_\beta$.

270 MHz ^{1}H NMR spectrometer, two doublet methyl signals coalesced at 52 °C, whereas with a 90 MHz spectrometer, they coalesced at 35.5 °C. Since the difference in the chemical shifts of the methyl peaks in δ value is 0.448, we obtained 64.7±0.2 kJ mol^{-1} for $\Delta G^{\neq}$ at 52 °C and 64.1±0.2 kJ mol^{-1} for $\Delta G^{\neq}$ at 35.5 °C from the Eyring Eq. 1,[34]

$$k = \varkappa(k_b T/h)\exp(-\Delta G^{\neq}/RT), \quad (1)$$

where k, the rate constant of enantiotopomerization, is $2^{-1/2}\pi\Delta\nu$ and $\Delta\nu$ is the chemical-shift difference of the two exchanging nuclei, represented in Hz. Accordingly, 52.9±8.1 kJ mol^{-1} and −36.5±24.2 J K^{-1} mol^{-1} for $\Delta H^{\neq}$ and $\Delta S^{\neq}$ of **2E**, respectively, were derived.

In order that a **2E** molecule isomerizes to its enantiomer, the furan ring must pass by the isopropylidene group by way of an extremely crowded transition state. There are two possible enantiotopomerization ways. One pathway may occur between *P*-**2E**$_\alpha$ and *M*-**2E**$_\alpha$, where the 2-methyl group (Me(15)) on the furan ring passes by the *E*-methyl group (Me(18)) of the isopropylidene group. The other (path ii) may occur between *M*-**2E**$_\beta$ and *P*-**2E**$_\beta$, where the C(11) hydrogen on the furan ring passes by Me(18). Consequently, the activation enthalpy values of these two processes were calculated by the AM1 molecular-orbital calculation method. Although it seems that path i from *P*-**2E**$_\alpha$ would give *M*-**2E**$_\alpha$, the dihedral angle of the furan rotation of the transition state is close to that of *M*-**2E**$_\alpha$; therefore, this process gives *P*-**2E**$_\beta$ directly (Fig. 7). Since there is a thermal equilibration between *P*-**2E**$_\beta$ and *M*-**2E**$_\alpha$ (the enantiomeric version of isomerization between *M*-**2E**$_\beta$ and *P*-**2E**$_\alpha$), *P*-**2E**$_\alpha$ could enantiotopomerize to give *M*-**2E**$_\alpha$ in two steps. The calculated $\Delta H^{\neq}$ value for path i is 67.3 kJ mol^{-1}, while that for path ii is 51.5 kJ mol^{-1} (Fig. 7). Since the latter is smaller and is in good accordance with the value obtained from ^{1}H NMR experiments (52.9±8.1 kJ mol^{-1}), we concluded that the enantiotopomerization of furylfulgide **2E** occurs mainly between *M*-**2E**$_\beta$ and *P*-**2E**$_\beta$. A schematic diagram of the conformational changes

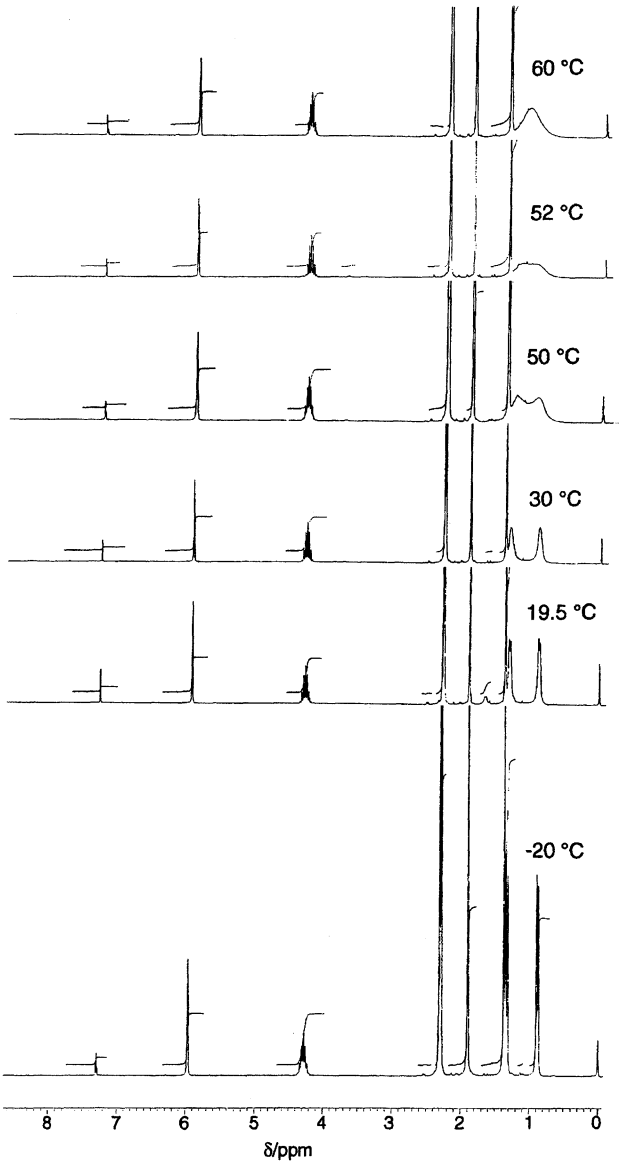


Fig. 6. Variable-temperature ^{1}H NMR spectra of **2E** in $CDCl_3$ (270 MHz).

of **2E** is shown in Fig. 8.

The activation enthalpy values of interconversion from *P*-**2E**$_\alpha$ to *M*-**2E**$_\beta$, and *M*-**2E**$_\alpha$ to *P*-**2E**$_\beta$, are calculated to be 10.4 kJ mol^{-1}, and that from *M*-**2E**$_\beta$ to *P*-**2E**$_\alpha$ and from *P*-**2E**$_\beta$ to *M*-**2E**$_\alpha$ are 9.3 kJ mol^{-1}. Since these barriers are low, the enantiotopomerization between *P*-**2E**$_\alpha$ and *M*-**2E**$_\alpha$ occurs in three steps, by way of *M*-**2E**$_\beta$ and *P*-**2E**$_\beta$. The easiness of interconversion between *P*-**2E**$_\alpha$ and *M*-**2E**$_\beta$ and between *M*-**2E**$_\alpha$ and *P*-**2E**$_\beta$ is rationalized that it occurs like the "belly roll" of a high jump: The furan ring faces its "belly" toward Me(18) throughout the conformational change.

Experimental

The syntheses of **1E** and **2E** were performed according to procedures mentioned in the literature.[12]

X-Ray diffraction measurements were made on a Rigaku AFC5 diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71069 Å). The integrated intensities were corrected for Lorentz

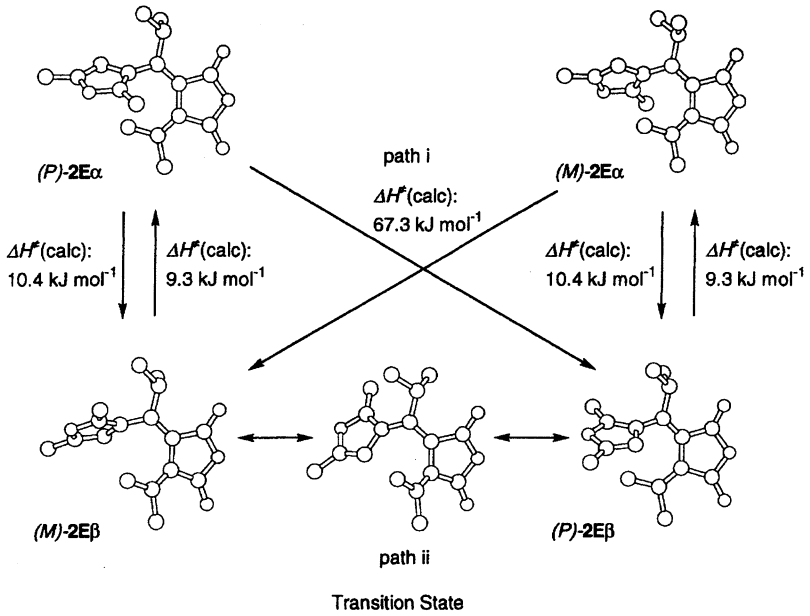


Fig. 7. Conformational change of **2E**.

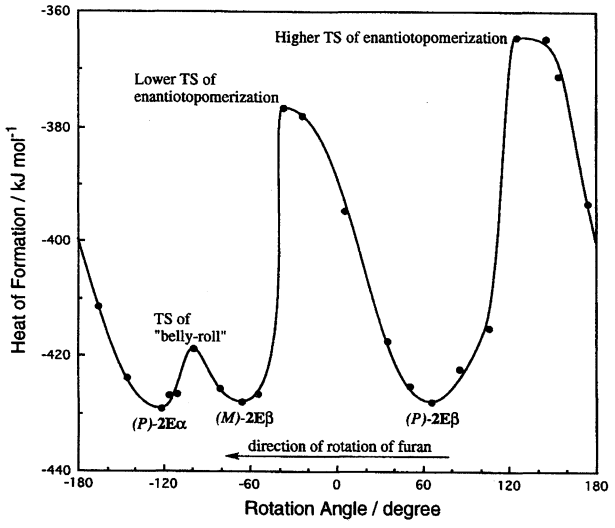


Fig. 8. Plots of H_f vs. rotation of dihedral angle of C(1)–C(8)–C(10)–C(11) of **2E**.

and polarization effects, but not for absorption. The structures were solved by a direct method using Shelxs 86,[35] and then refined by a full-matrix least-squares method using Shelxl 93[36] (**1E**) or Shelx 76[37] (**2E**). All of the hydrogen atoms were located by difference maps and refined isotropically. All of the non-hydrogen atoms were refined anisotropically. Calculations of the geometrical parameters and the drawings of ORTEP diagrams were performed by the XTAL system.[38] Full details concerning the crystallographic analyses are described in supplementary materials.[39]

Crystallographic data for **1E**: $C_{15}H_{16}O_4$, MW=260.28, pale-yellow crystal obtained from $CDCl_3$ solution, monoclinic, space group $P2_1/n$, Z=4, T=296 K. a=12.574(1), b=7.798(3), c=14.797(1) Å, β=109.384(9)°, V=1368.6(6) Å^3. R=0.074 and S=1.168 for observed reflections ($F_o \geq 2\sigma_F$).

Crystallographic data for **2E**: $C_{17}H_{20}O_4$, MW=288.34, pale-yellow crystal obtained from hexane–ether solution, monoclinic, space group $P2_1/c$, Z=4, T=296 K. a=8.201(1), b=19.037(2), c=10.772(1) Å, β=110.64(1)°, V=1573.8(4) Å^3. R=0.064 and S=1.647 for observed reflections ($F_o \geq 3\sigma_F$).

NMR measurements were carried out with JEOL FX-90Q (90 MHz) and JNM-EX-270 (270 MHz) spectrometers for variable-temperature measurements, GE-NMRI OMEGA400WB (400 MHz, for INADEQUATE and C-H COSY measurements), and Bruker DMX-500 (500 MHz, for NOE experiments) spectrometers, in $CDCl_3$.

AM1 molecular-orbital calculations were performed on a HITAC M-280D VOS3/ES1, The University of Tokyo.

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