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A Molecular Orbital Study of Conformational Behavior of 9,9′-Bifluorenylidene

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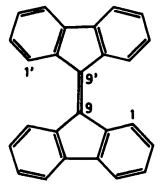
The conformation of 9,9′-bifluorenylidene and the $E \rightarrow Z$ isomerization of its derivatives were examined by a two-configuration SCF calculation with the MINDO/3 approximation. The twisted conformation was calculated to be more stable than the folded one. The E–Z isomerization occurs between two twisted conformers and the 90°-twisted structure is the transition state. The structural dependence of the rotational barrier of the isomerization is discussed.

Bifluorenylidene, **1**, is a highly overcrowded ethylene[1] and is expected to exist in one of the two possible conformations, the twisted or folded conformation, in order to avoid large repulsive interactions around the central C_9–$C_{9'}$ double bond. In the twisted form,



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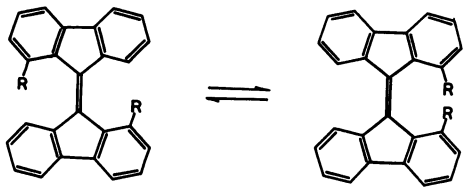
the two 9-fluorenylidene fragments make a large twist angle but maintain planarity. In the folded form, the fragments are folded away from each other without rotation about the C_9–$C_{9'}$ bond. The Newman projections of these two structures are shown in Fig. 1.

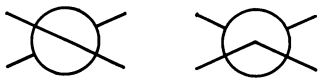
Gault et al.[2] assumed in their NMR study of substituted 9,9′-bifluorenylidenes in solution that the compounds existed in folded forms. In the solid state, an X-ray analysis showed that **1** has the twisted conformation with approximately planar 9-fluorenylidene fragments.[3] The substituted 9,9′-bifluorenylidenes have a barrier of 80—100 kJ mol^{-1} for a rotation about the C_9–$C_{9'}$ double bond in the E–Z isomerization.[4,5] These values are remarkably low in comparison with the rotational barrier of ethylene, 273 kJ mol^{-1}.[6]

Conformations and the E–Z isomerization of 9,9′-bifluorenylidenes have been studied by molecular



E **Z**

mechanics calculations.[7,8] As a molecular orbital calculation on 9,9′-bifluorenylidene, Meyer and Yinnon employed the π-electron calculation method to estimate the twist angle of 40°.[9] The present study examined the conformation of **1** on the basis of all-valence-



(a) (b)

Fig. 1. Newman projections of 9,9′-bifluorenylidene. (a) Twisted form and (b) folded form.

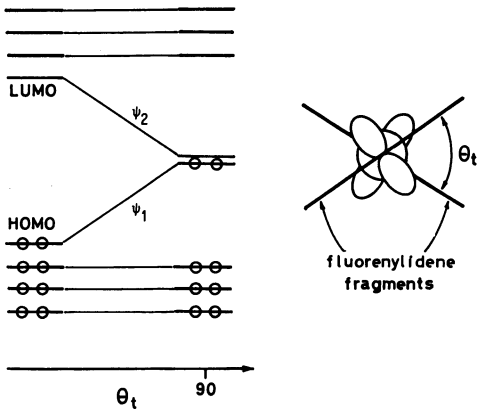


Fig. 2. Qualitative variation of orbital energies of 9,9′-bifluorenylidene with the twist angle about the central C–C double bond. The ψ_1 and ψ_2 orbitals are the bonding and anti-bonding π-orbitals of the ethylenic double bond, respectively.

electron MO calculations and analyze the E–Z isomerization process of substituted 9,9′-bifluorenylidenes.

Method

The electronic structure of the 90°-twisted 9,9′-bifluorenylidene can not appropriately be calculated by the closed-shell SCF method. It can be treated by the method applied to 10,10′-bianthrone.[10] As the twist angle about the 9–9′ double bond of 9,9′-bifluorenylidene increases, the energy separation between the bonding (ψ_1) and antibonding (ψ_2) π-orbitals associated with the C_9–$C_{9'}$ double bond decreases (Fig. 2). In the 90°-twisted 9,9′-bifluorenylidene, the ψ_1 and ψ_2 orbitals are degenerate, and the two closed-shell configurations, Φ_1 and Φ_2, contribute equally to the lowest singlet state.

$$\Phi_1 = |\cdots\psi_1\bar{\psi}_1|$$

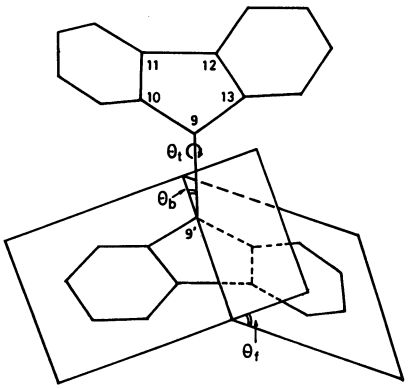


Fig. 3. Molecular parameters which represent the 9,9′-bifluorenylidene structure. For the six-membered ring, C-C=1.418 Å, C-H=1.084 Å, and all the valence angles=120° were fixed in the calculation.

and

$$\Phi_2 = |\cdots\psi_2\overline{\psi}_2|.$$

Thus, 9,9′-bifluorenylidene with a large twist angle should be calculated by two-configuration SCF (TCSCF) wave function,

$$\Phi_G = C_1|\cdots\psi_1\overline{\psi}_1| + C_2|\cdots\psi_2\overline{\psi}_2|. \quad (1)$$

9,9′-Bifluorenylidene is too large in size for ab initio calculations and the MINDO/3 approximation[11] was used. A small model compound cannot be used for the present purpose, since the conformational behavior of 9,9′-bifluorenylidene is essentially controlled by steric interactions. Only a part of molecular structure was optimized. The parameters are shown in Fig. 3. These parameters were determined by using a closed-shell SCF calculation. The TCSCF method was used for the energy calculation when the twist angle was changed from 0 to 90° and the other parameters were fixed at the optimized values.

In order to understand the energy change associated with the conformational change, the total energy of the TCSCF wave function was divided into three parts,

$$E_{total} = E_1 + E_2 + E_{1-2},$$

where E_1 and E_2 are the energies of two 9-fluorenylidene fragments and E_{1-2} is the inter-fragment energy between the two fragments.

Results and Discussion

The molecular structures are listed in Table 1. The calculated values of the twisted form agree well with experimental values.[3] The variations in the energy vs. the twist angle are shown in Fig. 4. The most stable conformation of 9,9′-bifluorenylidene was a twist form with θ_t=45°. This agrees with the structures in solid state[3] and of molecular mechanics calculations.[8] The lowest folded form has θ_t=0° and lies 27 kJ mol^{-1} above the twisted conformation. Table 2 shows the energy components in the twisted and folded forms. The energy of each 9-fluorenylidene fragment is lower in the twisted form by 58 kJ mol^{-1} due to the planarity of the fragments maintained in the twisted form. On the other hand, the interaction energy between two fragments, E_{1-2}, is lower in the folded form by 89 kJ mol^{-1}. This comes from the favorable resonance interaction between the C_9 and $C_{9'}$ atoms in the folded form; this stronger interaction can be seen in the shorter C_9-$C_{9'}$ bond in the folded form.

Table 1. Structure Parameters of Folded and Twisted Forms of 9,9′-Bifluorenylidene in Their Lowest Energy Conformations[a]

Parameter[b]	Folded	Twisted	Exp. (twisted)[c]
$R_{9-9'}$	1.381	1.392	1.377
R_{9-10}	1.538	1.529	1.48 — 1.49
α	53.1	51.9	52.5 — 53.4
β	108.4	109.4	106.7—109.5
θ_t	0	45.0	43
θ_f	27.7	0	0
θ_b	14.8	0	0

a) Bond lengths are in Å and bond angles are in degrees. b) α is the half of the C_{10}-C_9-C_{13} angle and β is the C_{11}-C_{10}-C_9 angle which are measured before folding the 9-fluorenylidene fragment. c) Ref. 3.

Table 2. Energy Components in the Folded and Twisted Structures

	Twisted(θ_t=45°)	Folded(θ_t=0°)	ΔE/kJ mol^{-1}
E_1	−1754.218 eV	−1753.619 eV	58
E_2	−1754.218	−1753.619	58
E_{1-2}	−17.990	−18.914	−89

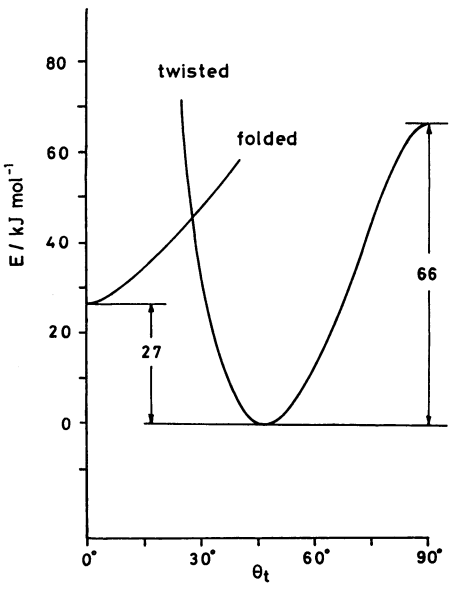
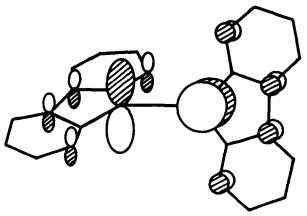


Fig. 4. Potential energy curves of 9,9′-bifluorenylidene with the twist angle θ_t. The energy is relative one with respect to the lowest twisted structure.



π_1 π_2

Fig. 5. Two π-orbitals of 9-fluorenylidene fragments. The ψ_1 and ψ_2 orbitals for $\theta_t=90°$ in Fig. 2 are expressed by linear combination of these two π-orbitals.

The contribution of the second configuration in Eq. 1 to the Φ_G wave function was 4—6% when $\theta_t \leqq 50°$. It increased when $\theta_t \geqq 60°$ and reached 50% at $\theta_t=90°$. The wave function of the 90°-twisted structure was, thus,

$$\Phi_G = \frac{1}{\sqrt{2}}|\cdots\psi_1\bar{\psi}_1| - \frac{1}{\sqrt{2}}|\cdots\psi_2\bar{\psi}_2|, \quad (2)$$

where the ψ_1 and ψ_2 orbitals were expressed by π_1 and π_2 orbitals each of which belongs to one of

$$\psi_1 = \frac{1}{\sqrt{2}}(\pi_1+\pi_2)$$
$$\psi_2 = \frac{1}{\sqrt{2}}(\pi_1-\pi_2) \quad (3)$$

the orthogonal 9-fluorenylidene fragment (Fig. 5). By using Eq. 3, Eq. 2 can be expressed in terms of the π_1 and π_2 orbitals by

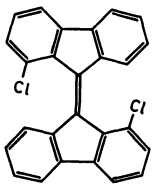
$$\Phi_G = \frac{1}{\sqrt{2}}\{|\cdots\pi_1\bar{\pi}_2| + |\cdots\pi_2\bar{\pi}_1|\},$$

indicating that the lowest singlet state of the 90°-twisted 9,9′-bifluorenylidene is a diradical in which the two orthogonal π_1 and π_2 orbitals are occupied by unpaired electrons.

The present calculations show that *E*–*Z* isomerization is an interconversion between two twisted forms via the transition state of the 90°-twisted conformation. This is an interesting contrast with the *E*–*Z* isomerization of 10,10′-bianthrone where the 90°-twisted structure is not the transition state.[10,12] The barrier to the isomerization of 9,9′-bifluorenylidene was shown to be 66 kJ mol^{-1}, which is somewhat smaller than the value estimated from experiments, 108 kJ mol^{-1}.[13] Two factors need to be considered in an elucidation of structural effects on the low barrier for *E*–*Z* isomerization. First is the ground-state destabilization due to the steric repulsion around the 9–9′ bond, and the second is the stabilization of the diradical transition state by a large conjugated system. These two factors were examined by using the 1,1′-dichloro derivative, **2**, and the benzo-annelated compound, **3**. Table 3 shows the calculated energies of *E*-twisted, *Z*-twisted, and 90°-twisted structures of **2** and **3**. In the compound **2**, the *E*-form is more stable than the *Z*-form by 7 kJ mol^{-1}. This agrees with the experimental facts that in the 1,1′-disubstituted 9,9′-bifluorenylidenes, the *E*-form is more stable than the *Z*-form by 2—4 kJ mol^{-1}.[4,5] The activation energy calculated for the *E*→*Z* isomerization of **3**, 65 kJ mol^{-1}, is larger than that of **2**, 43 kJ mol^{-1}: this is parallel to the experimental findings.[4,5] The lowering of the rotational barrier by the introduction of chlorine atoms at the 1,1′-positions is attributed to the higher repulsion between fragments. This was reflected in the large twist angle, 53°, and was confirmed by the energy components analysis.

Table 3. Relative Energies of Conformers and the 90°-Twisted Structure of 9,9′-Bifluorenylidenes

Compound	Conformation	θ_t	Energy/kJ mol^{-1}
1	Twisted	45°	0
	90°-twisted	90°	66
2	*E*	53°	0
	Z	58°	7
	90°-twisted	90°	43
3	*E*	45°	0
	Z	45°	0
	90°-twisted	90°	65



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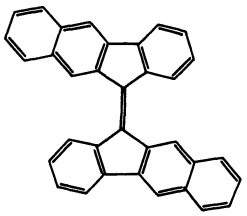

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The extension of the conjugated system is considered to stabilize the transition-state diradical and lower the barrier for the *E*–*Z* isomerization.[5] However, the lowering of the activation energy calculated for **3** was very small, 1 kJ mol^{-1}. The ground state is also expected to be stabilized by extension of the conjugated system, and the benzo-annelation stabilizes both the ground state and the transition state in the same extent.

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