

Theoretical Investigation on the Origin of the CD Signal Reversal for the Closed-ring Isomer of Diarylethene with Peripheral π -Conjugated Substituents

Takashi Hirose,^{1,2} Jun-ya Hasegawa,¹ and Kenji Matsuda*^{1,2}

¹Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510

²Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 744 Motoooka, Nishi-ku, Fukuoka 819-0395

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Theoretical investigation was performed on the CD signal of the closed-ring isomer of diarylethene with an extended π -conjugated substituent. The result showed that the different contribution of the substituent to the transition electronic and magnetic dipole moments induces CD signal reversal. The obtained finding can be applied to general dyes with a chiral core and extended π -conjugated substituents.

Diarylethenes are representative photochromic compounds which convert their structures upon irradiation with an appropriate wavelength of light between the open- and the closed-ring isomer.¹ The closed-ring isomer of a diarylethene has two enantiomers that are (*R,R*) and (*S,S*) isomers originating from the two asymmetric carbon atoms.² Optical resolution has been carried out for several diarylethenes and the CD spectra of them have been reported. Yokoyama et al. reported the CD spectra of the closed-ring isomers of 1,2-bis(5-hydroxymethyl-2-methyl-3-thienyl)hexafluorocyclopentene (**1**) (Chart 1).³ The sign of the Cotton effect in the visible region was reported to be positive for the (*R,R*) isomer. Meanwhile, the signs of the Cotton effect of the following diarylethenes **2**,⁴ **3**,⁵ and **4**,⁶ have been reported to be negative for the (*R,R*) isomers. The phenyl substituent at 5-position of the thiophene ring is supposed to be important for the reversal of the CD signal, but the effect of the substituent has not been understood yet. In this paper, we will describe the theoretical investigation of the effect of the extended π -conjugated substituent on the CD signal.

The intensity of the CD signal of the transition from $|\varphi_i\rangle$ to $|\varphi_f\rangle$ is described by the rotatory strength that is the imaginary part of the inner product of the transition electronic dipole moment $\mathbf{E} = e\langle\varphi_i|\mathbf{r}|\varphi_f\rangle$ and the transition magnetic dipole moment $\mathbf{M} = (-ie\hbar/2mc)\langle\varphi_f|\mathbf{r} \times \nabla|\varphi_i\rangle$ by the following equation.

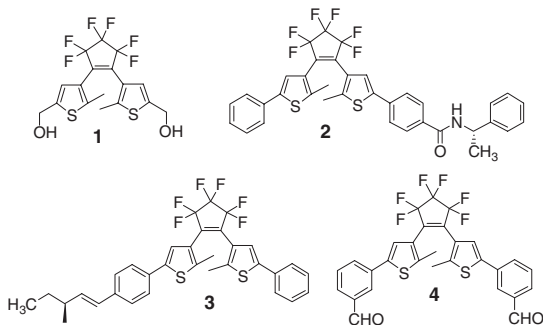


Chart 1.

$$R = \text{Im}(\mathbf{E} \cdot \mathbf{M}) = \text{Im}(\mathbf{E}_X \mathbf{M}_X + \mathbf{E}_Y \mathbf{M}_Y + \mathbf{E}_Z \mathbf{M}_Z) \quad (1)$$

When two moments are perpendicular, for example, when the molecule is completely planar, there is no CD signal observed.

We calculated the transition electronic and magnetic dipole moments for the lowest-energy transition and derived the CD signal for the following five diarylethenes **5–9** for the (*R,R*) isomer (Chart 2). The transitions are mainly HOMO–LUMO transitions. Calculation was carried out at TD DFT B3LYP/6-31G* level of theory. The molecules were fragmented to inner chiral core and outer π -conjugated substituents and their contributions to the transition electronic and magnetic dipole moments \mathbf{E} and \mathbf{M} were calculated.⁷

Figure 1 shows the HOMO and LUMO of the closed-ring isomer **9** along with the molecular axis *x*, *y*, and *z*. The HOMO is antisymmetric with respect to the *yz* plane and antisymmetric to the *xy* plane. The LUMO is symmetric to the *yz* plane and antisymmetric to the *xy* plane. The symmetry consideration

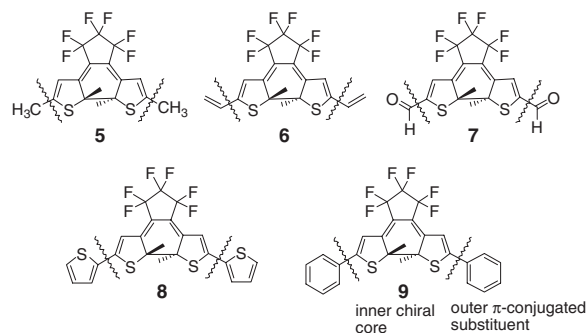


Chart 2.

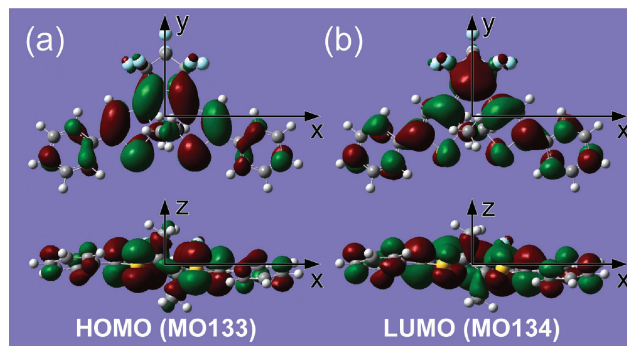


Figure 1. Orbital shapes of (a) HOMO and (b) LUMO of the closed-ring isomer **9**.

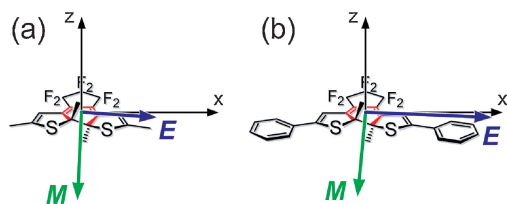


Figure 2. Transition electronic and magnetic moments of (a) **5** and (b) **9**.

Table 1. Calculated rotatory strengths and their components

Cmpd	$E_X M_X^a$	$E_Y M_Y^a$	$E_Z M_Z^a$	Rotatory strength	$ E ^b$	$ M ^c$
5	-32.71	0.19	51.66	19.15	4.160	1.765
6	-18.55	0.04	36.47	17.96	6.105	1.376
7	-46.37	0.11	36.01	-10.26	5.150	1.501
8	-104.69	0.13	35.68	-68.88	8.131	1.436
9	-117.81	0.11	50.08	-67.62	7.383	1.696

^a 10^{-40} erg·esu·cm/gauss. ^b 10^{-18} esu·cm (=Debye). ^c 10^{-20} erg/gauss.

predicts that the transition electronic dipole moment \mathbf{E} corresponding to the absorption from the HOMO to LUMO is located parallel to the x axis of the molecule and the transition magnetic moment \mathbf{M} is located parallel to the z axis. Chirality on the core tilts \mathbf{E} from the x axis to $-z$ direction and \mathbf{M} from the z axis to $-x$ direction, which results in the appearance of the CD signal (Figure 2).

Table 1 summarizes the calculated results. The rotatory strength changes sign from positive to negative when the π -conjugated substituent is larger than vinyl. When the π -conjugated substituent gets large, the $E_X M_X$ component gets negatively large but the $E_Z M_Z$ component remains almost constant at certain positive values. $E_Y M_Y$ does not show significant contribution. The absolute value $|E|$ gets large but $|M|$ remains almost constant. The calculation results show that when the π -conjugated substituent gets large, $E_X M_X$ component gets large to induce CD signal reversal.

In order to get more information on this behavior, calculations were performed on the fragment of the molecule to separate the contribution from the outer substituent. The results are summarized in Table 2. The contribution from the substituent to transition electronic moment \mathbf{E} is significant on x -component $E_{X(\text{Sub})}$, but not on z -component $E_{Z(\text{Sub})}$. For the transition magnetic moment \mathbf{M} , the contribution from the substituent is very small for any direction.

Figure 1 also shows that the orbital shapes of the phenyl substituents in the HOMO and LUMO are almost identical though there is difference in phase. The transition is mainly characterized by the inner core. Because $\langle \psi | \mathbf{r} \times \nabla | \psi \rangle = 0$ for any real wave functions $\langle \psi |$, the identical orbitals of the substituents in the HOMO and LUMO give no contribution to the transition magnetic moment \mathbf{M} in principle. Therefore, in all the cases, the values of $M_{X(\text{Sub})}$, $M_{Y(\text{Sub})}$, $M_{Z(\text{Sub})}$ are considered to be very small. The extended substituents are almost coplanar to the molecular plane, so that the extension of the π system contributes to the increase of the transition electronic dipole moment \mathbf{E} in the x -direction, the direction of the original transition moment. The z -component E_Z originates from the tilting by the chiral core, so that the extension does not

Table 2. Calculated transition electronic and magnetic dipole moments

Cmpd	x -components					
	E_X (Core)	E_X (Sub)	E_X	M_X (Core)	M_X (Sub)	M_X
5	2.306	1.844	4.150	-0.087	0.008	-0.079
6	1.888	4.212	6.100	-0.058	0.027	-0.030
7	1.917	3.228	5.144	-0.066	-0.025	-0.090
8	1.620	6.507	8.127	-0.115	-0.013	-0.129
9	1.892	5.486	7.377	-0.137	-0.022	-0.160
Cmpd	y -components					
	E_Y (Core)	E_Y (Sub)	E_Y	M_Y (Core)	M_Y (Sub)	M_Y
5	-0.033	-0.004	-0.036	-0.051	-0.002	-0.053
6	0.017	-0.007	0.010	0.045	-0.001	0.044
7	0.019	0.004	0.023	0.044	0.003	0.047
8	0.026	0.007	0.033	0.035	0.005	0.040
9	0.024	0.001	0.025	0.035	0.009	0.044
Cmpd	z -components					
	E_Z (Core)	E_Z (Sub)	E_Z	M_Z (Core)	M_Z (Sub)	M_Z
5	-0.343	0.050	-0.293	-1.785	0.022	-1.763
6	-0.257	-0.009	-0.265	-1.620	0.245	-1.375
7	-0.316	0.075	-0.240	-1.572	0.074	-1.498
8	-0.309	0.059	-0.250	-1.642	0.212	-1.429
9	-0.336	0.040	-0.297	-1.744	0.055	-1.688

contribute to this direction (Figure 2). The different contribution of the substituent to the x -, y -, and z -components of \mathbf{E} and \mathbf{M} is attributed to the induction of the CD signal reversal. This result can be applied to general dyes carrying chiral core and extended π -conjugated substituents, warning that the CD signal reversal does not always mean the reversal of the chiral core.

In conclusion, the CD signal reversal observed for the closed-ring isomer of the diarylethene with extended π -conjugated substituent was rationally explained. The different contribution of the substituent to the transition electronic and magnetic dipole moments is important for the CD signal reversal. This finding can be applied to general dyes with a chiral core and extended π -conjugated substituents.

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References and Notes

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