A Microscopic Model for Helical Twisting Power by the Optical Isomers of an Octahedral Metal Complex

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A computational approach to the evaluation of helical twisting powers (HTP) of chiral metal complexes of [Ru(blade)$_2$(backbone)] type is presented. The dopant contains helically attached "blade" ligands and an elongated "backbone" ligand, and some remarkably powerful examples have been reported. In this work, the observed HTP is interpreted in terms of a microscopic interaction of a dopant and host molecules with atomistic details. For this purpose, the stable structure of a triad system comprising a dopant and two host molecules was obtained by geometry optimization using Gaussian03. As a result, the host molecules interacted attractively with the dopant, being twisted in the same direction as observed experimentally. Interaction energy was assessed as a function of the dihedral angle between the two host molecules, leading to a quadratic dependence with a minimum at the equilibrium twisting angle of $-32°$. Based on this, the expression was derived, in which helical twisting power was given in terms of the equilibrium twisting angle of a pair of strongly interacting host molecules. [DOI: 10.1143/JJAP.44.4067]

KEYWORDS: *ab initio*, chiral dopant, metal complex, helical twisting power

1. Introduction

Chirality is an important factor in liquid crystal technology.[1] It is well-known that a nematic phase (host) transits to a chiral nematic phase, when a small amount of chiral molecules (dopant) are dissolved. Capability of such a dopant effect is expressed in terms of helical twisting power (HTP; denoted as β) as defined below:[2]

$$\beta = \left(\frac{\partial P^{-1}}{\partial X} \right)_{x \to 0} \qquad (1)$$

where P^{-1} is the inverse of a pitch and x the molar fraction of a dopant. In order to develop a dopant with high β, it will be of vital importance to reveal the relation of β with its molecular structure. As far as we know, there have been reported several works predicting a helical twisting power by studying the molecular surface of a dopant.[3–12] According to refs. 3 and 4 the alignment of a dopant molecule is determined by the interaction of its chiral surface with a locally nematic medium. No specific interaction, however, between a dopant and host molecules is taken into account.

Recently we have been interested in the $\Delta\Lambda$-isomerism of transition metal complexes as a source of chirality in liquid crystals.[13,14] It is reported that Δ-[Ru(acac)$_2$L], in which L and acac denote a mesogenic derivative of 4,4′-bipyridine (or 5,5′-(4-octyphenyl-oxycarbonyl)-2,2′-bipyridyl), and acetylacetonate ligands, respectively, gives an extremely high β ($-180\,\mu m^{-1}$) when it is doped in N-(4-methoxy-benzylidene)-4-n-butylaniline (MBBA). The high value of β for these molecules may be related to the presence of the host molecules which interact strongly with a dopant molecule. The large twisting of such host molecules may exert a torque, inducing the sequential twist of other host molecules. In order to examine such a possibility, we have performed the theoretical simulation on the microscopic structure in the vicinity of a dopant molecule. It was attempted to elucidate a simple model for helical twisting power on the basis of the strongly attractive interaction between the host and dopant molecules.

2. Calculation Method

The interaction of a dopant with host molecules was studied by calculating the configuration of a triad system consisting of Δ-[Ru(acac)$_2$L] and two MBBA molecules. For simulation, it was assumed that the potential energy of a dopant molecule was determined by the intermolecular interaction of a dopant and two host molecules.

Several typical cases were selected as an initial configuration of hosts around the dopant by placing two host molecules. The rod-like ligand L in Δ-[Ru(acac)$_2$L] was expected to assist the dopant's orientational ordering. Therefore, while one of the two host molecules (denoted by *molecule A*) was laid *along* the long axis of L in the calculations, the other (denoted by *molecule B*) was positioned at the chiral void space between the two acac ligands.

At first, a dopant molecule was assumed to be Δ-[Mg(acac)$_2$L] with no d-electron instead of Δ-[Ru(acac)$_2$L] with six d-electrons. This was because the contribution of d-electrons to interaction energy was expected to be negligible. The interaction of ligands of a dopant with MBBA was thought to be a main factor in stabilizing the system. The geometry optimization of the system was performed at the HF/3-21G** level for [Mg(acac)$_2$L] with the Gaussian03 program.[15] The association energy (ΔE) was calculated with reference to the energy of a system consisting of dummy atoms corresponding to either a dopant or hosts. Calculation was made by using "*Counterpoise*" command. ΔE was obtained using HF/6-31G** by the following equation:

$$\Delta E = E \text{ (hosts and a dopant)}$$
$$- E \text{ (hosts and a dummy dopant)} \qquad (2)$$
$$- E \text{ (dummy hosts and a dopant)}$$

After such an optimization procedure, the energy of the triad system was calculated by varying the twisting angle or the dihedral angle of O–N–O–N of two host molecules. This

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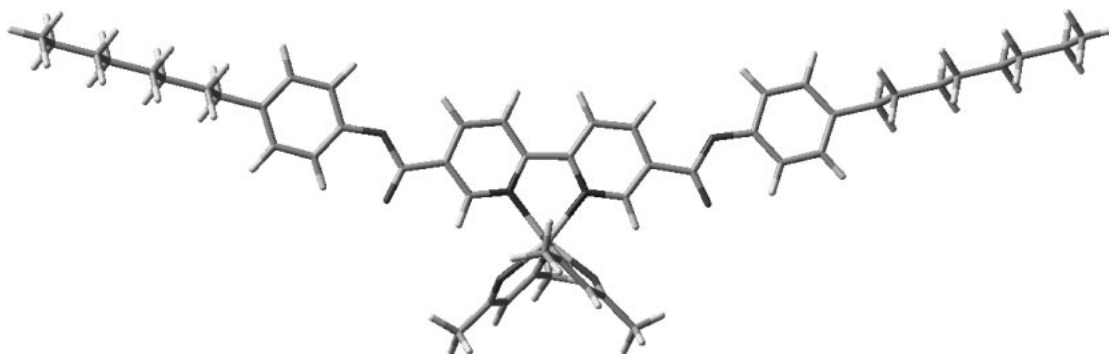
Fig. 1.   The optimized molecular structure of Δ-[Ru(acac)₂L].
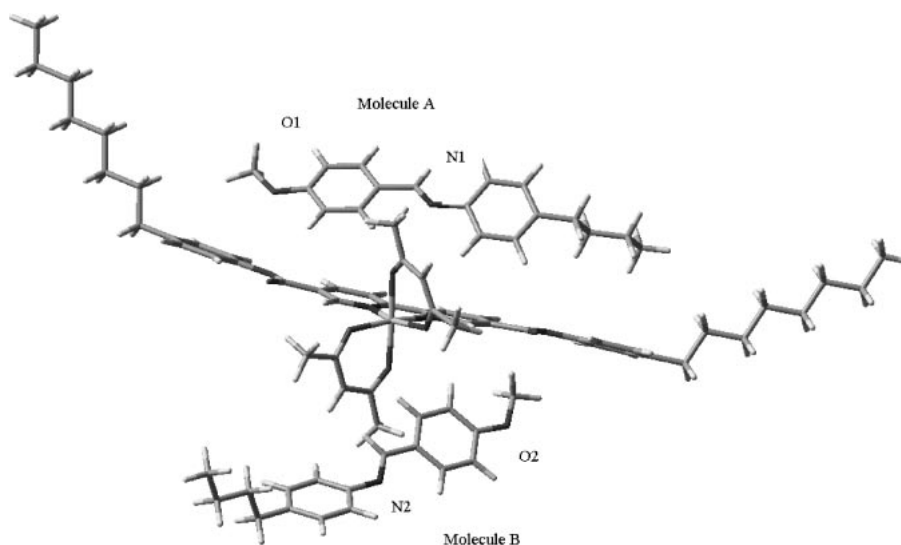
Fig. 2.   The optimized structure of the triad system consisting of Δ-[Ru(acac)₂L] and two MBBA molecules.

time, more precise energy was calculated for [Ru(acac)₂L] in which HF/LANL2DZ was used for Ru(II) atom and HF/6-31G** for other atoms. Here *molecule B* rotated around an axis connecting its molecular center and an Ru atom of the dopant with *molecule A* fixed. The energy as a function of the dihedral angle thus obtained was regarded as a potential energy curve for the twisting of two host molecules at the vicinity of a dopant.

3.   Results

The geometrical optimization was performed for the triad system of one dopant and two host molecules. Here the dopant molecule (Δ-[Ru(acac)₂L]) was assumed to take the orientation in which the long axis of L oriented in the direction of the nematic director of host medium. Figure 1 shows the optimized structure of the dopant (Δ-[Ru(acac)₂L]). Figure 2 shows an example of the stable configuration for the triad system under such orientation. The dihedral angle of two hosts (O–N–O–N) was estimated to be $-32°$, being taken to be less than $90°$. The twisting direction of these two host molecules was coincident with the left-handed helicity as observed for the chiral nematic phase induced by Δ-[Ru(acac)₂L]. The association energy of MBBA molecules with the dopant was obtained to be $-18\,\mathrm{kJ\,mol^{-1}}$ according to eq. (2). Figure 3 shows the
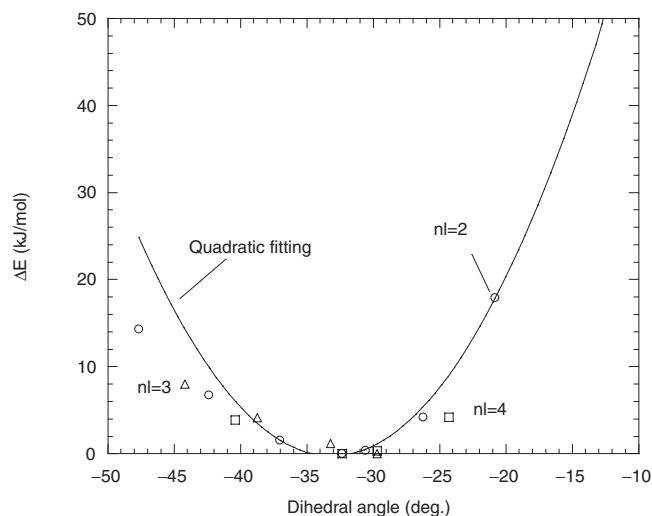

Fig. 3.   The dependence of potential energy on the dihedral angle of two MBBA molecules. The potential curve was plotted as a function of a twisting angle of *molecule B* around the dopant when the distances between the host molecules and the dopant were fixed. The value of n_l was taken to be 2 (○), 3 (△) and 4 (□). The solid curve corresponded to the quadratic fitting.

calculated potential curve as a function of the dihedral angle of two MBBA molecules. The distances between hosts *molecules (A or B)* and a dopant were fixed at the value corresponding to the optimized structures. As shown in the figure, the potential curve takes a minimum value in the range of -30 to $-37°$.

The computational results revealed that two MBBA molecules associated with Δ-[Ru(acac)$_2$L] twisted in the same direction as observed in the experiments.[14] The most stable twisting ($2\theta_e$) was, however, far greater in size than the average twisting angle ($\hat{\theta}$) of a host in a bulk medium. For example, the value of $\hat{\theta}$ is only $-0.04°$ per a molecular dimension (0.4 nm) for a typical case of $p = -3.3\,\mu\text{m}$ at $x = 0.6\%$ for our dopant.[14] In order to obtain the helical twisting power from the present simulation results, it is necessary to relate the large twist in the vicinity of a dopant to the thermally averaged twist in a bulk medium.

We approximate the host molecules as cylinders, and a chiral nematic phase consisting of stacked slices of nematic layers of thickness d. Let those which are distant from a dopant molecule (denoted by *host 0*) twist by the averaged angle, $\hat{\theta}$, and those which are in contact with the dopant (denoted by *host 1*) twist by an arbitrary angle of θ (Fig. 4). It should be noted here that θ differs from θ_e, because *host 1* molecules may be partially unwound by their neighboring *host 0* molecules. A set of parameters on the molecular scale are defined for convenience as each of the twist angles divided by the molecular thickness (d):

$$\hat{q} = \hat{\theta}/d$$
$$q_e = \theta_e/d \qquad (3)$$
$$q = \theta/d$$

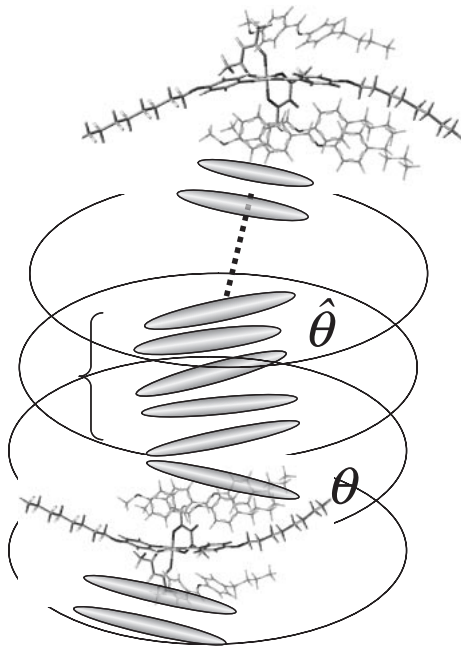The free energy of the system is then given by the following equation:

Fig. 4.   The schematic drawing for the association of host molecules with a dopant. The molecules (*host 1*) in the vicinity of the dopant twist by the large angle of θ, while the molecules (*host 0*) apart from the dopant twist by the small angle of $\hat{\theta}$.

$$F(q, \hat{q}) = N_\text{d}f(q) + \frac{1}{2}n_l N_\text{d}\hat{K}'_{22}(q - \hat{q})^2 + \frac{1}{2}N_\text{h}\hat{K}'_{22}\hat{q}^2 \quad (4)$$

Here, the first term is the stabilization energy of a dopant molecule interacting with *host 1* molecules in which N_d denotes the number of dopants. The third term gives the twist deformation energy of *host 0* molecules ($\hat{K}'_{22} = \hat{K}_{22}/d^2$). The second term is introduced to account for the excess torsional energy accumulated at the boundary between *host 0* and *host 1* molecules, the number of which is designated by n_l. For the potential curve of $f(q)$, the simulation results as shown by Fig. 3 are applied, in which the curve is approximated by the following quadratic form:

$$f(q) = \frac{\alpha}{2}(q - q_e)^2 - \frac{\alpha}{2}q_e^{\,2} \qquad (5)$$

Here a parameter, α corresponds to the curvature of the calculated potential curve in the vicinity of $q = q_e$.

The equilibrium helical state is determined by minimizing the free energy in eq. (4) with respect to the variation of both $\hat{q}$ and q. It is necessary to know the relation between $\hat{q}$ and q. Such a relation should be sought by solving how a large twist generated near a dopant exerts a torque over distances through a bulk chiral nematic medium.[16] The calculation seems to be beyond the present work. Instead, the relation between $\hat{q}$ and q was simply derived on the assumption of the local winding and unwinding equilibrium to take the minimum of the first and second terms in eq. (4) for the variation of q at a fixed value of $\hat{q}$:

$$\frac{\partial}{\partial q}\left(N_\text{d}f(q) + \frac{1}{2}n_l N_\text{d}\hat{K}'_{22}(q - \hat{q})^2\right) = 0 \qquad (6)$$

Equation (6) leads to the following relation:

$$q = \frac{\alpha q_e + n_l\hat{K}'_{22}\hat{q}}{\alpha + n_l\hat{K}'_{22}} = \frac{q_e + \phi\hat{q}}{1 + \phi} \qquad (7)$$

In other words, q is a weighed average of q_e and $\hat{q}$. The weighting factors may be handled more easily by introducing their ratio ϕ as below.

$$\phi = \frac{n_l\hat{K}'_{22}}{\alpha} \qquad (8)$$

We consider two extreme cases depending on the magnitude of ϕ.

Case 1: $\phi \ll 1$. This is a situation where *host 1* molecules are trapped deeply in the dopant's potential. Under this condition, we obtain

$$q = (1 - \phi)q_e + \phi\hat{q} \qquad (9)$$

The total free energy in eq. (4) was minimized with respect to the variation of $\hat{q}$, leading to the following result:

$$\frac{\partial F}{\partial \hat{q}} = -\alpha\phi^2(q_e - \hat{q})N_\text{d} - n_l N_\text{d}\hat{K}'_{22}(1 - \phi)^2(q_e - \hat{q})$$
$$+ N_\text{h}\hat{K}'_{22}\hat{q} = 0 \qquad (10)$$

Or

$$N_\text{h}\hat{K}'_{22}\hat{q} = \alpha\phi^2(q_e - \hat{q})N_\text{d} + n_l N_\text{d}(1 - \phi)^2(q_e - \hat{q})\hat{K}'_{22}$$
$$= \alpha(q_e - \hat{q})N_\text{d}(\phi^2 + \phi(1 - \phi)^2) \qquad (11)$$
$$\cong \alpha\phi(q_e - \hat{q})N_\text{d}(1 - \phi)$$

Neglecting the terms of the first order of ϕ, the following equation is derived for β:

$$\beta = \frac{(1-\phi)}{2\pi} \frac{n_l \theta_e}{d} \approx \frac{n_l}{2\pi d} \theta_e. \qquad (12)$$

Case 2: $\phi \gg 1$. This extreme corresponds to a shallow potential, and hence only a weak rewinding.

$$q = \frac{1}{\phi} q_e + \hat{q} \qquad (13)$$

Under this relation, the second term in eq. (4) is constant as

$$\frac{1}{2} n_l N_d \hat{K}'_{22} \left(\frac{1}{\phi}\right)^2 q_e^2.$$

Thus minimization was performed by neglecting the second term for the variation of $\hat{q}$. This leads to the final equation for β as below:

$$\beta = \frac{\theta_e}{2\pi \hat{K}'_{22} d} \alpha \qquad (14)$$

Equation (14) is coincident with the usual mean field formulations based on the continuum model.[3]

$$\beta = \frac{1}{2\pi \hat{K}'_{22}} \left(\frac{\partial f(q)}{\partial \hat{q}}\right)_{\hat{q}=0}, \qquad (15)$$

since

$$\left(\frac{\partial f(q)}{\partial \hat{q}}\right)_{\hat{q}=0} = \frac{\alpha \theta_e}{d}. \qquad (16)$$

The magnitude of parameter ϕ was estimated for the present system as below. According to our molecular modeling, at least two host molecules bind strongly as shown in Fig. 2. Thus n_l is taken to be 2 as the minimum value, and $\hat{K}'_{22} = 7.9 \times 10^{-21}$ N m (for MBBA from ref. 3) and $\alpha = 2.6 \times 10^{-18}$ N m (from Fig. 3). Inserting these values to eq. (8), ϕ is calculated to be 0.006. This value is much less than unity, leading to the conclusion that the present case should be described as Case 1 ($\phi \ll 1$). Inserting $d = 0.45$ nm (typical breadth of aliphatic chains in liquid crystals) and $2\theta_e = -32°$ into eq. (12), β is calculated to be $-200\,\mu\text{m}^{-1}$.

In estimating the probable value of n_l, we took $n_l = 2$ as a first choice. This value was chosen on the assumption that the upper and lower host molecules around a dopant would be most strongly influenced by the helical nature of the dopant. We also made further simulation for the case of $n_l = 3$, in which three MBBA molecules were placed in contact with a host as nearest neighbors [Fig. 5(a)]. All host molecules were found to twist largely. The dihedral angle was obtained to be $-29°$ or $-26°$ for pairs of A/B or A/C, respectively. Taking into account the variation of the dihedral angle and n_l (2–3) as the error range, β was estimated to take a value of -200 to $-275\,\mu\text{m}^{-1}$.

In order to see the possibility of $n_l > 3$, we made simulation for the system in which two MBBA molecules (denoted by A and B) and one MBBA molecule (denoted by C) were placed in direct contact with a dopant and one additional MBBA molecule (denoted by D) was placed in the vicinity of one of the alkyl chains. The optimization was performed for various initial distances of a dopant and a MBBA molecule (D), while the positions of other three

MBBA molecules (A, B, C) were fixed at the optimized structures as were already determined for the case of $n_l = 3$. As a result, it was found that a MBBA molecule (D) was little effected by the interaction with a dopant as shown in Fig. 5(b). The twisting angle ($2\theta_e$) between a MBBA molecule (D) and its nearest neighbors [a MBBA molecule (A and D)] was obtained to be less than $-3.0°$, respectively. Thus we concluded that only the host molecules that were in direct contact with a dopant molecule were twisted by a large amount, contributing to the stability of the system according to eq. (4). In order others, the probable value of n_l would be 2–3.

In order to see the bulk effect on the potential curve of a dopant, we performed simulation containing the system involving one dopant and four MBBA molecules. It was aimed to see the effect of additional MBBA molecules on the potential curve of a dopant. Two MBBA molecules (C) and (D) were placed under a MBBA molecule (B). A MBBA molecule (A) was placed above the dopant. The positions of MBBA molecules (C) and (D) were optimized while those of MBBA molecules (A) and (B) and the dopant were fixed. The potential curve was calculated by twisting a MBBA molecule (B) around the dopant when MBBA molecules (A), (C) and (D) were fixed. As shown in Fig. 3, the value of α was little affected by the presence of the additional MBBA molecules. Thus we concluded that other remote molecules (MBBA molecules C and D) influenced little on the potential curve of a dopant. We regarded the results as evidence supporting the small effect of a bulk medium on the potential curve of a dopant.

Based on these results, we concluded that the probable value of n_l would be 2–3. β was calculated as -200 to $-275\,\mu\text{m}^{-1}$. The estimated β was larger than the experimentally observed β ($-180\,\mu\text{m}^{-1}$).[14] Considering that the orientational fluctuation was not considered so far, the calculated β was regarded as an upper limit of the experimental behavior.

4. Discussion

The present model based on the local structure around a dopant reproduces well the upper limit of β for the present system. For a comparison, β for the same system is estimated on the basis of the continuum medium theory (or the Ferrarini model).[3,4] In this model, the orienting potential for chiral solutes is treated as the interaction with the solvent as below;

$$U(\Omega) = \varepsilon_{an} \int dS [3(\mathbf{d} \cdot \mathbf{s})^2 - 1]/2 \qquad (17)$$

in which the proportionality constant, ε_{an}, is the orienting strength, $\mathbf{d}$ the nematic director vector and $\mathbf{s}$ the unit vector orthogonal to a surface element dS, and Ω the parameter describing the orientation of a dopant, respectively. An appropriate averaging of $U(\Omega)$ leads to a so-called "chirality order parameter" Q in their formulation of β:

$$\beta = \frac{\varepsilon_{an}}{2\pi \hat{K}_{22}} \mathsf{Q} \qquad (18)$$

The principal axis system of the ordering tensor has been shown in Fig. 6. The anisotropic content of Q is expressed by eq. (19), into which also the orientational information can
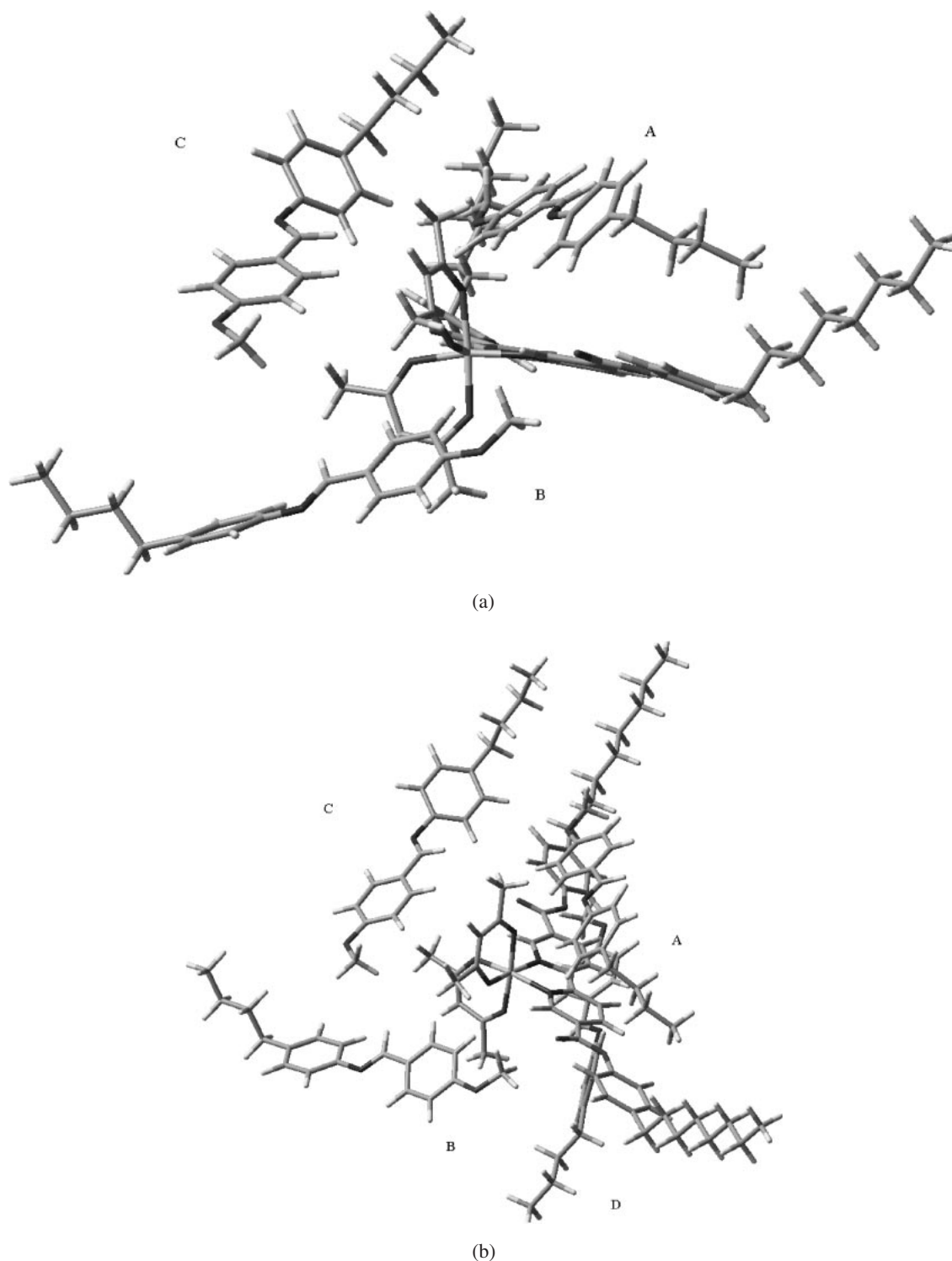
(a)

(b)

Fig. 5.　The optimized structure of (a) three hosts (denoted by A, B and C) and a dopant in case of $n_l = 3$ and (b) four hosts (denoted by A, B, C and D) and a dopant in case of $n_l = 4$.

be input.

$$Q = -\sqrt{\frac{2}{3}}(Q_{xx}S_{xx} + Q_{yy}S_{yy} + Q_{zz}S_{zz}) \qquad (19)$$

The terms of Q_{ii}'s are the corresponding components of the surface chirality tensor.

$$Q_{ii} = 2 \times \sqrt{\frac{3}{8}} \int s_i(\hat{s} \times \boldsymbol{r})_i \, dr, \qquad (20)$$

in which $\boldsymbol{r}$ is a vector giving the position of a point on the molecular surface and $\hat{s}$ the unit vector pointing normal to the surface. Three components of Q_{ii} for Λ-and Δ-[Ru(acac)$_2$L] can be estimated by:

$$Q_{xx} = \pm\frac{\sqrt{3}}{2} \times V, \quad Q_{yy} = 0, \quad Q_{zz} = \mp\frac{\sqrt{3}}{2} \times V, \quad (21)$$

where the upper and lower signs correspond to the Λ- and Δ-enantiomers, respectively. V represents the area of an acac ligand (approximated as flat) multiplied by the distance
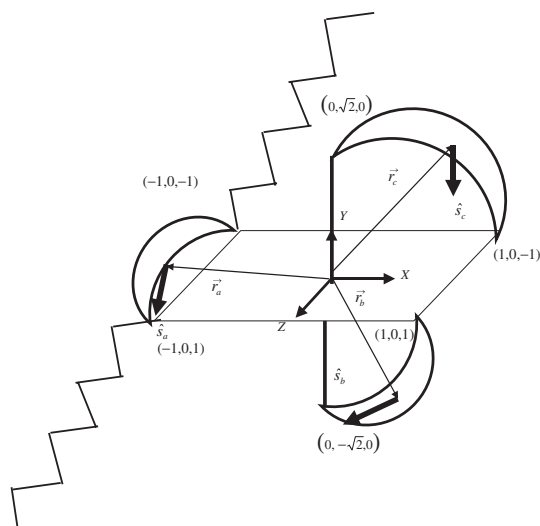
Fig. 6. Geometrical parameters of Δ-[Ru(acac)₂L] assumed to calculate the tensor components of Q.

between a central Ru(II) atom and the center of acac ligand. When V is estimated to be about $0.45\,\text{nm}$ (Ru(II)–acac distance) $\times 0.62\,\text{nm}$ (long axis of acac) $\times 0.26\,\text{nm}$ (short axis of acac) $= 0.072\,\text{nm}^3$ from Fig. 1, the elements of the surface chirality tensor are obtained to be $Q_{xx} = \pm 0.062\,\text{nm}^3$ and $Q_{zz} = \mp 0.062\,\text{nm}^3$. Assuming that the complex orients uniaxially with $S_{zz} = 0.7$, for instance, the HTP is calculated to be $\pm 110\,\mu\text{m}^{-1}$ for the Λ- and Δ-enantiomers, respectively, using values of $\varepsilon_{\text{an}}/k_B T = 5\,\text{nm}^{-2}$ and $\hat{K}_{22} = 1.6 \times 10^{-39}\,\text{N m}^3$ ($K_{22} = 3.2 \times 10^{-12}\,\text{N}$ and the molar volume of MBBA $= 3.0 \times 10^{-4}\,\text{m}^3$) as suggested in ref. 3. Thus the Ferrarini model leads to the reasonable value for the HTP of the present type of dopant, although the estimated value is 40% smaller than the experimental one.

When the above two models on the derivation of helical twisting power are compared, the following aspects are to be noted:

(1) In the Ferrarini model, the host is assumed to be continuum medium and the twisting of a local director is very small. In fact, expression (18) is obtained as a limit of $\hat{\theta}$ to zero.[3] In contrast, the present computational results on the microscopic structure around a dopant analogue have revealed far greater twist (of the same parity as experimental results) in the locus of the metal center. More notably, the potential energy curve (Fig. 3) shows that the state in which two MBBA molecules are parallel with each other (or $\hat{\theta} = 0$) is over $100\,\text{kJ mol}^{-1}$ less stable than the state in which they twist at the potential minimum ($2\theta_e$). Thus it is of urgent need to have information as to the orientation of host molecules in the vicinity of a dopant to judge which of the above models reflects more precisely the real circumstances.

(2) According to eq. (12), β is expressed in terms of three

parameters, n_l, d and θ_e. All these parameters are related to the microstructure of the local system involving a dopant and strongly interacting host molecules (*host 1*). The torsional effect between the largely twisted host molecules (*host 1*) and the slightly twisted host molecules (*host 0*) is an essential factor in determining β.

Our approach sheds light on the local molecular effect around the dopant. Although the shape model accounts for the dopant performance generally very well and also in the present case, it is not always feasible to numerate elements of the surface chirality tensor, particularly for flexible molecules. While existing theories for the chiral phase inductions seem to furnish fair conclusions on the equilibrium states, most of the molecular interactions of chemical interests are often far too coarsened. Our approach given above may find applicability to a wide range of molecular systems, as it may suffice to compute the potential energy curve for a cluster of liquid crystal molecules twisted around a dopant. The criterion for its utility would be that the curvature must dominate over bulk elastic constant.

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