714 © 1993 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 66, 714—720(1993) [Vol. 66, No. 3

Molecular Mechanics Studies on the Ligand Conformation of Chiral Ruthenium Tris(2,2′-bipyridine)-Type Complexes

Hitoshi Ishida, Taisuke Hamada, Yu-ichi Fujishita, Yuri Saito, and Katsutoshi Ohkubo*
Department of Applied Chemistry, Faculty of Engineering, Kumamoto University, Kumamoto 860

(Received September 10, 1992)

Molecular mechanics (MM) calculations were performed for two chiral ligands, 4,4′-bis[*R*(or *S*)-phenylethylamino carbonyl]-2,2′-bipyridine (*R*(or *S*)-PhEtbpy) and 4,4′-bis(menthoxycarbonyl)-2,2′-bipyridine (Menbpy) by the MM2PRIME program with several new parameters. These ruthenium complexes have been already found to be efficient catalysts for photochemical and enantioselective electron transfer reactions. The bonded terms in the new parameters were determined by Hopfinger's method with molecular orbital (MO) calculations. The MO calculations were mainly performed with AM1 program, however some torsional parameters were also determined by ab initio MO methods to compare with the results derived by semi-empirical methods. The electrostatic parameters were determined with the AM1 program by using the electrostatic potential (ESP) method. To find the most stable conformation, the contour maps of the strain energy of the chiral ligands were drawn as a function of rotation of the chiral groups, and the favorable conformation obtained was supported by ^{1}H NMR measurement. The structures of these ruthenium complexes were also discussed on the CD spectra of the complexes and the enantioselectivity of the reaction.

Stereoselectivity in photochemical[1,2] and thermal[3] electron transfer reactions between metal-ion complexes in solutions have received considerable interest with particular reference to the electron transfer mechanism and the transition state structures. In many reports about stereoselective electron-transfer reactions, the report by Porter et al. is important as the first example of enantioselective and photo-induced electron transfer between transition metal complexes; Δ-[Ru(bpy)$_3$]$^{2+}$ (bpy=2,2′-bipyridine) reduced Λ-[Co(acac)$_3$] (acacH= acetylacetone) preferentially with the reaction rate ratio of 13 to 12 toward the Λ and Δ forms.[1a] However, it was not a catalytic system, because the ruthenium complex racemized rapidly under irradiation, and the catalytic system for enantioselective electron transfer was as yet unknown.

We have reported the first catalytic system of the enantioselective and photo-induced reductions of [Co(acac)$_3$] by the ruthenium tris(bipyridine)-type complexes, [Ru{*R*(or *S*)-PhEtbpy}$_3$]$^{2+}$ and [Ru(Menbpy)$_3$]$^{2+}$ (Fig. 1).[2] The complexes have the chiral groups, *R*(+)(or *S*(−))-1-phenylethylaminocarbonyl and (1*R*,2*S*,5*R*)-(−)-menthoxycarbonyl, at 4,4′-positions in the 2,2′-bipyridine type ligands, respectively. From the CD spectra, [Ru(Menbpy)$_3$]$^{2+}$ is racemic for molecular asymmetry (Δ and Λ),[2a] however [Ru{*R*(or *S*)-PhEtbpy}$_3$]$^{2+}$ has not only chirality in the ligands but also molecular asymmetry; *R*(+) and *S*(−)-PhEtbpy induced Δ and Λ-configuration predominantly for the ruthenium complexes, respectively.[2b] Interestingly, [Ru(*R*-PhEtbpy)$_3$]$^{2+}$ which had Δ-configuration reduced Δ-[Co(acac)$_3$] predominantly. This finding seems to conflict with Porter's report: Δ-ruthenium complex reduced Λ-cobalt complex preferentially.

The purpose of this article is to explain the question of the conformation of the ruthenium complexes based on molecular mechanics (MM) calculations. However, the calculations of the ligands required new parameters due to a lack of bonded parameters for the pyridine ring and carboxyl groups connected with pyridine. We have determined the force-field parameters with semi-empirical molecular orbital (MO) calculations by using the methods of Hopfinger et al.[4] This method may be too simple, however, the most stable structure obtained by the force-field mechanics is reliable and useful for the purpose of the present investigation. The energy barrier for the conformational changes is also considered to be qualitatively reliable.

In this paper, we describe the force-field parameters obtained from the semi-empirical MO calculations. We performed partly ab initio MO calculations in comparison with the semi-empirical ones. Subsequently, energy contour maps were drawn for the chiral group orientation in the ligands to search the most stable conformation. The ^{1}H NMR spectrum of the ligand was measured to support the result obtained by the MM analyses. Finally, we will discuss the plausible structures of the ligands and the ruthenium complexes and the reason why the Δ-ruthenium complex reduces the Δ-cobalt complexes predominantly.

Experimental

The molecular mechanics calculations in this study were performed with the program MM2PRIME implemented on a FACOM M-780/10Q.[5] Total energy is expressed as a sum of the bonded term (bond, bond angle, and dihedral angle) and the nonbonded term (van der Waals and electrostatic) in Allinger's force fields. The parameters for the bonded terms were derived from molecular orbital calculations using the method of A. J. Hopfinger et al.[4] In this method, one first selects model compounds containing the structural unit whose parameters in bonded terms are needed. The bond length, angle, and torsional force-field functions are presented by Eqs. 1, 2, and 3,

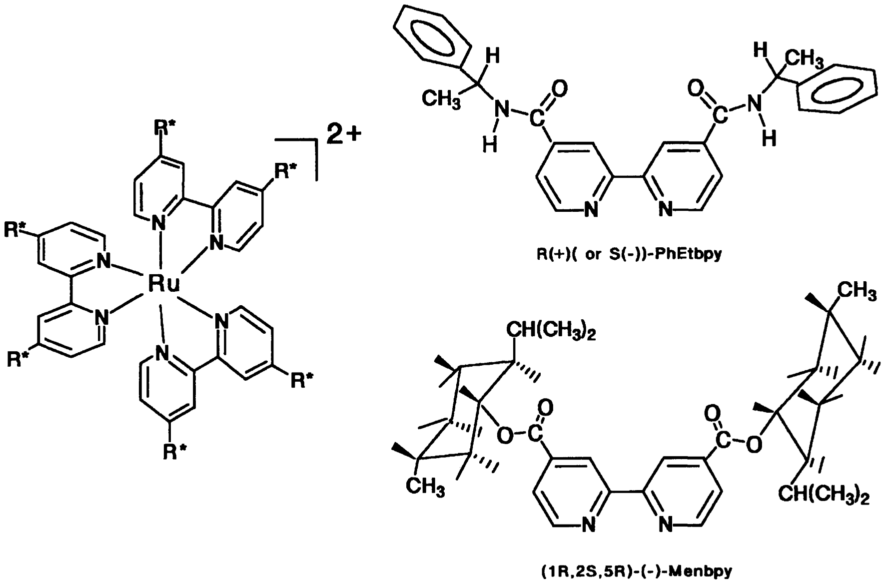


Fig. 1. Chiral ligands, *R*(or *S*)-PhEtbpy and Menbpy, and its ruthenium tris(bipyridine)type complexes.

$$E_l = k_l\,(l - l_0)^2\,, \tag{1}$$

$$E_\phi = k_\phi\,(\phi - \phi_0)^2\,, \tag{2}$$

$$E_\theta = V_1/2(1+\cos\theta) + V_2/2(1-\cos 2\theta) + V_3/2(1+\cos 3\theta), \tag{3}$$

in which l and l_0 are bond length and equilibrium bond length, ϕ and ϕ_0 are bond angle and equilibrium bond angle, and θ is torsion angle. We selected the model compounds as shown in Fig. 2 and performed the molecular orbital calculations of them in order to determine the bonded parameters. The calculations were performed with the program MOPAC ver. 6.0 (AM1),[6] and a part of the parameters were compared with those derived by ab initio (at the 6-31G basis set) method with the program GAUSSIAN 82.[7]

The nonbonded terms of the parameters consist of van der Waals and electrostatic interactions, and these functions are presented by Eqs. 4 and 5,

$$E_{\rm vdw} = \varepsilon^*\left(2.9\times10^5\exp\left(-12.5R/r^*\right) - 2.3\left(r^*/R\right)^6\right), \tag{4}$$

$$E_{\rm ele} = 332.4\left(q_iq_j/\varepsilon R\right), \tag{5}$$

where ε^* is hardness of atom, r is van der Waals radii ($r^* = r_i + r_j$), R is interatomic distance, and q is fractional charge. The new atom type (No. 29) was set as pyridine nitrogen, however the van der Waals parameters of the atom type used the same values as the other nitrogen's values, that is, ε^* and r^* values were 0.055 kcal mol^{-1} and 1.820 Å, respectively. Electrostatic parameters were calculated by electrostatic potential (ESP) method with the program AM1.

The stable conformations were searched by drawing contour maps of the total energies of the ligands as a function of rotation of the chiral groups. The energy was calculated at the torsion angles by varying these angles by every 15° and minimizing the total energy for each torsion angle.

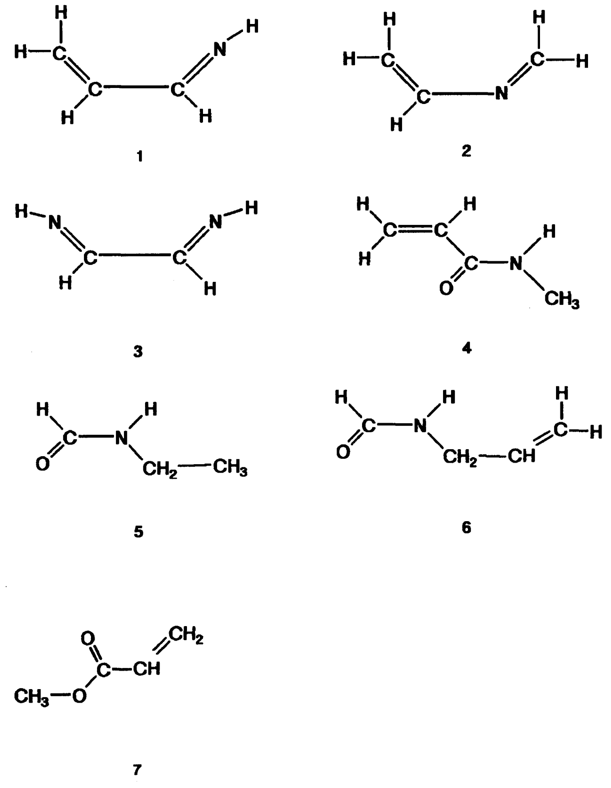


Fig. 2. Model compounds for MO calculations to determine bonded parameters.

^{1}H NMR measurement of *R*(+)-PhEtbpy. The chiral ligand, R(+)-PhEtbpy, was prepared by the method which had been already reported.[2b)] ^{1}H NMR spectrum of the ligand was measured by JEOL JNM-GX400. ^{1}H NMR (400 MHz, DMSO-d_6) δ=1.54 (d, 6H, CH$_3$), 5.24 (m, 2H, CH), 7.25 (2H, *p*-phenyl), 7.36 (4H, *m*-phenyl), 7.43 (4H, *o*-phenyl), 7.90 (d, 2H, pyridine H$_5$, H$_{5'}$), 8.84 (s, 2H, pyridine H$_3$, H$_{3'}$), 8.89 (d, 2H, pyridine H$_6$, H$_{6'}$), 9.35 (d, 2H, amide N–H, $J_{{\rm HN}_\alpha}$=8.1 Hz).

Table 1. Bond Length and Angle Parameters Determined by AM1 Method

Parameters[a)]	Model molecule	Equilibrium values[b)]	Force constants[c)]
C2–N29	1	1.330	17.017
C3–N9	4	1.486	8.879
C2–C2–N29	1	127.882	1.705
H5–C2–N29	1	115.061	1.161
C2–N29–H5	1	116.769	0.846
C2–N29–C2	2	123.836	1.366
C2–C3–O6	7	129.114	1.755
C2–C3–N9	4	115.760	2.262
O7–C3–N9	4	122.359	2.264
C3–N9–C1	4	117.756	1.189
C3–N9–H5	4	117.896	1.188
C1–N9–H5	5	117.780	1.168
N9–C1–H5	5	108.166	1.134
N9–C1–C1	5	114.100	1.767
N9–C1–C2	6	114.812	1.760

a) C1: carbon (CSP3); C2: carbon (CSP2, alkene); C3: carbon (CSP2, carbonyl); H5: hydrogen; O6: ester oxygen; O7: carbonyl oxygen; N8: nitrogen (NSP3); N9: nitrogen (NSP2); N29: pyridine nitrogen (new atom). b) Angstrom (Å) and degree for bond length and angle parameters, respectively. c) Unit form of force constants are mdyn Å^{-1} and mdyn Å rad^{-2} for bond length and angle parameters, respectively.

Results and Discussion

Molecular Mechanics Force Field Parameterization for the Chiral Ligands. The parameters for molecular mechanics calculation are required in the bonded (bond, angle, and dihedral) and the nonbonded (van der Waals and electrostatic) terms. The bonded terms in the parameters were determined with MO calculations of the model compounds using the method of Hopfinger et al.[4)] The parameters obtained by the MO calculations of the model compounds in Fig. 2 are listed in Tables 1 and 2. The bond and angle parameters in the bonded terms estimated seem to be accurate even with semi-empirical MO calculations. However, the torsional parameters determined by the MNDO method often give incorrect results, for example, π-conjugated compounds (such as benzaldehyde or nitrobenzene) tend to be stable as nonplaner structures. AM1 is generally known to overcome the weakness of MNDO, however uncertainty in the results of semi-empirical MO calculation remains. To check whether there is no inversion of the stable structure, we calculated two rotational barriers for one of the model molecules with ab initio MO calculation (6-31G basis set). Figure 3 shows both results of AM1 and ab initio MO calculation, and they have an essentially similar tendencies though the barriers obtained by ab initio calculations are somewhat higher than ones by the AM1 program. The torsional parameters (V_1, V_2, V_3) obtained from the ab initio calculations are 3.312, 3.061, 2.085 for C_2–C_2–C_3–N_9 and 4.462, 22.408, 1.300 for C_2–C_3–N_9–C_1, respectively.

Table 2. Torsional Angle Parameters Determined by AM1 Method

Parameters	Model molecule	Force constants[a)] V1	V2	V3
C2–C2–C2–N29	1	−0.442	1.141	0.445
C2–C2–N29–C2	2	−1.782	2.125	2.025
C2–C2–C3–O6	7	−0.147	2.262	0.188
C2–C3–O6–C1	7	11.623	2.613	1.930
C2–N29–C2–H5	2	3.538	0.108	−0.269
N29–C2–C2–N29	3	0.690	−0.542	0.344
N29–C2–C2–H5	1	1.640	0.330	0.032
C2–C2–C3–N9	4	1.580	−0.689	1.215
C2–C3–N9–H5	4	−0.537	21.164	0.401
C2–C3–N9–C1	4	1.680	19.462	0.736
C3–N9–C1–C1	5	0.524	2.293	−0.049
C3–N9–C1–C2	6	7.523	−2.128	1.102
C3–N9–C1–H5	5	−0.894	2.218	1.168
O7–C3–N9–C1	4	1.680	19.462	0.736
O7–C3–N9–H5	4	−0.540	21.163	0.404
H5–N9–C1–H5	4	0.276	0.301	−0.244
H5–N9–C1–C1	5	−1.803	0.791	2.487
H5–N9–C1–C2	6	−2.271	1.073	3.133
N9–C1–C1–H5	5	0.474	0.849	−0.077
N9–C1–C2–C2	6	1.544	−1.267	0.864

a) kcal mol^{-1}.

On the other hand, the parameters determined by the AM1 program are listed in Table 2. Since the differences between the parameters determined from ab initio calculations and AM1 are below about 4 kcal mol^{-1} and small, we used the AM1 program also in consideration of computational time.

Concerning the nonbonded terms, electrostatic parameters were determined by the AM1 program with electrostatic potential (ESP) option. The parameters obtained are depicted in Fig. 4. On the other hand, van der Waals parameters were used without any change from the standard values in Allinger's MM force field except for the pyridine nitrogen (see Experimental section).

Conformation of *R* (or *S*)-PhEtbpy and Menbpy. As the first step to discover the most stable conformation of *R* (or *S*)-PhEtbpy, we performed molecular orbital calculation of 4,4′-bis(methylaminocarbonyl)-2,2′-bipyridine which was a model molecule of PhEtbpy with AM1 program. It is considered to have several stable conformations, however the structures in which the nitrogen atoms of bipyridine lay in the trans-position are not important, because they are not permitted by the coordination to metal. In regard to amide structure, it is well-known that trans conformation is acceptable by X-ray analysis of peptides and theoretical studies. Therefore the next problem is whether the carbonyl oxygens are inside or outside of the molecule, however the latter is not considered to be favorable for steric hindrance, because the large chiral groups are close to each other. In fact, the MO calculations of these conformations of 4,4′-bis(methylaminocarbonyl)-2,2′-bipyr-

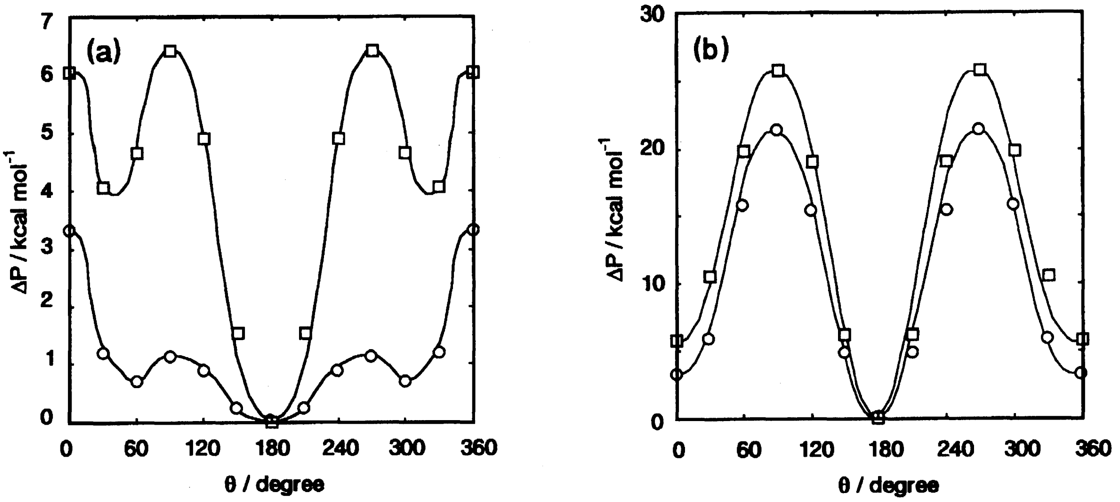
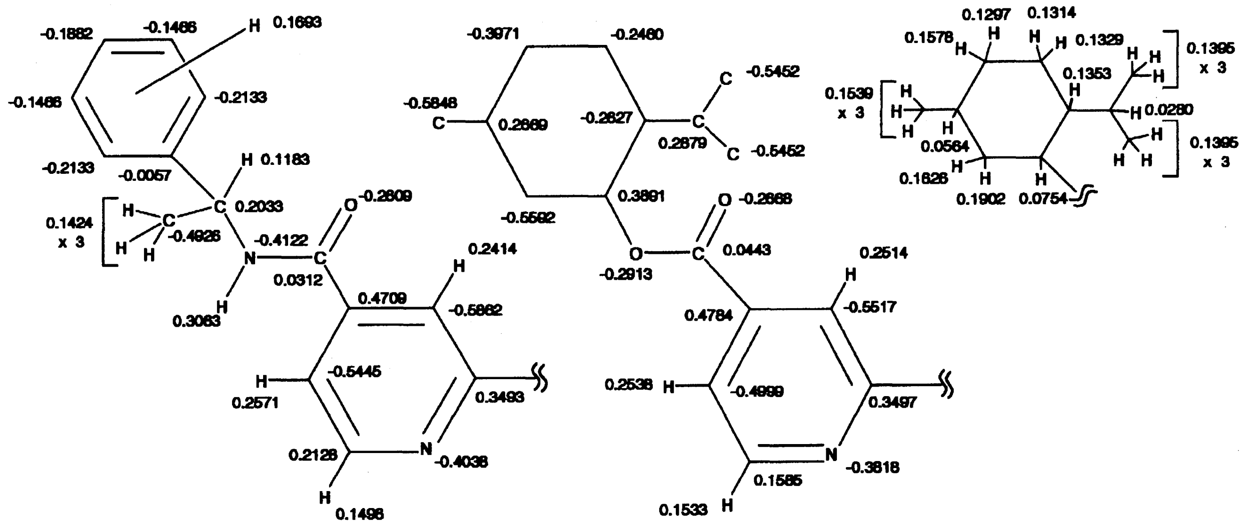


Fig. 3. Rotational barriers (a: C_2–C_2–C_3–N_9, b: C_2–C_3–N_9–C_1) of the model molecule 4 by AM1 (○) and ab initio MO calculations (□).



1-PhEtbpy

Menbpy

Fig. 4. Electrostatic parameters of the chiral ligands, *R* (or *S*)-PhEtbpy and Menbpy, determined by the AM1 program with ESP option.

idine resulted in 9.92 and 11.17 kcal mol^{-1} as the final heat of formation, respectively. Therefore, we further examined the ligand conformation in which the chiral groups are separated each other (that is, the carbonyl oxygen is inside of the molecule).

To find the most stable structure of *R* (or *S*)-PhEtbpy, we drew a contour map of the strain energies of the ligand as a function of rotation of the chiral group around the N–C_α bonds (ψ and ω). ψ and ω are defined for the angle C–N–C_α–C(Ar) as depicted in Fig. 5, which shows (ψ, ω)=(0, 0). The map and the most stable conformation (the ball and stick model: (ψ, ω)=(120, 120)) are also depicted in Fig. 5. The conformation has a symmetric axis between two pyridine nitrogens on a bipyridine plane. The left one of the phenyl rings of the ligand is above the bipyridine plane from the view of the metal ligated with the two pyridine nitrogens, and right one is below. The opposite conformation which has (ψ, ω)=(−120, −120) is not unstable, there is no local minimum point around there.

The most stable conformation was supported by a ^{1}H NMR spectrum of the ligand. The amide proton-C_α proton coupling constant, $^3J_{HN_\alpha}$, is known to vary in the torsional angle (θ) H–N–C_α–H from 2 to 10 Hz. The theoretical relation between the angle θ and the

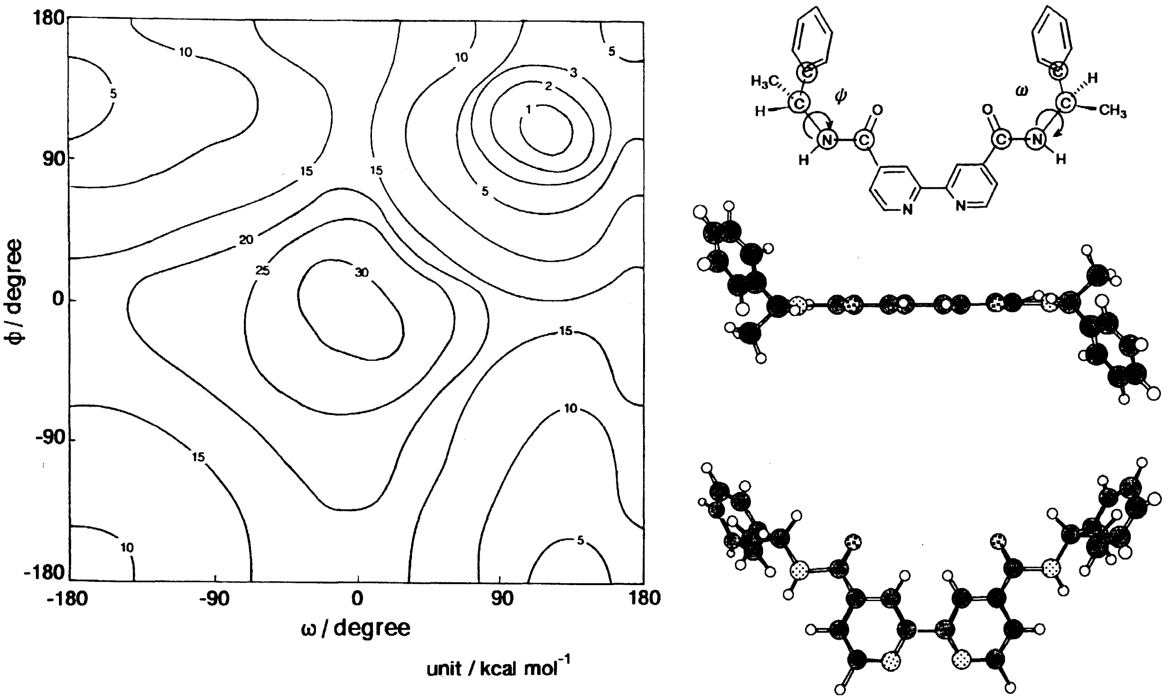


Fig. 5. Contour map of the strain energies of *R*-PhEtbpy as a function of the chiral group rotation about the N–C$_\alpha$ bonds (ψ and ω) and the most stable structure ((ψ, ω)=(120, 120)).

$^3J_{\mathrm{HN}_\alpha}$ value was described originally by Karplus,[8a,8b] however practical relation was examined for polypeptide chains (e.g., the globular protein basic pancreatic trypsin inhibitor (BPTI)) by Pardi et al.[8c] From the predictive information the $^3J_{\mathrm{HN}_\alpha}$ value of the ligand which we measured as 8.1 Hz (see Experimental section) gives that the θ value is considered to be around about 0° or 180°. The θ is related with ψ or ω by Eq., $\theta=\psi$ (or ω) $+60°$, therefore the values of ψ and ω are $-60°$ and $120°$. The most stable conformation ((ψ, ω)=(120, 120)) obtained by the MM calculation is consistent with the ^{1}H NMR result because the θ value is about 180°. The other symmetrical conformations having (−60, −60) and the unsymmetrical conformations such as (−60, 120) or (120, −60) as the (ψ, ω) set are clearly unstable from Fig. 5.

The stable conformation of Menbpy was similarly studied. The contour map of the strain energies of the ligand is depicted in Fig. 6. The ligand has two relatively stable conformations around (ψ, ω)=(30, 30) and (180, 0). In these conformations the apse lines of the menthyl group are approximately perpendicular to the bipyridine plane. The conformation around (30, 30) has two isopropyl groups of the menthyl groups at the opposite side, and one around (0, 180) at the same side. The former is relatively stable (the structure is depicted in Fig. 6), however the difference of the total energies is small and the barrier between the conformations is low compared with PhEtbpy. This is probably because ester bond can rotate more easily than amide bond. On the other hand, the barrier along a diagonal line on the map is relatively high. This exhibits that rotation of the chiral groups is difficult at the same time probably due to steric hindrance between the neighboring menthyl groups.

Proposed Structure of the Ruthenium Complexes Consisting the Chiral Ligands. The ruthenium tris(bipyridine)type complexes can be constructed based on the chiral ligand derived by MM analyses and the X-ray structure of ruthenium tris(2, 2′-bipyridine) dication complex.[9] The Δ and Λ forms of the ruthenium *R*-PhEtbpy complex are depicted in Fig. 7. The distances between phenyl rings of the neighboring ligands in these complexes are 14.1 and 10.0 Å for the Δ and Λ complexes, respectively, and Δ-[Ru(*R*-PhEtbpy)$_3$]$^{2+}$seems to be more stable than Λ form which has steric hindrance. In fact, the CD spectrum of the [Ru{*R*(or *S*)-PhEtbpy}$_3$]$^{2+}$ exhibited that the *R* and *S*-forms induced Δ and Λ-configuration, respectively.[2b] It is caused by steric hindrance between phenyl rings of the neighboring ligands in the complex. If the *R*-form of the ligand had the conformation of (−120, −120) at (ψ, ω), the result should be opposite: the complex of *R*-ligand should be favorably a Λ-configuration. In addition, if the *R*-ligand had the conformation, the $^3J_{\mathrm{HN}_\alpha}$ value should be smaller than 4 Hz because the θ value is about −60°.[8c] The rotation barrier is considerably high (ca. 20 kcal mol^{-1}), therefore there are probably no conformational changes in the ligand after complex formation.

We have already reported that Δ-[Ru(*R*-PhEtbpy)$_3$]$^{2+}$ catalyzes photo-induced and enantioselective reduction

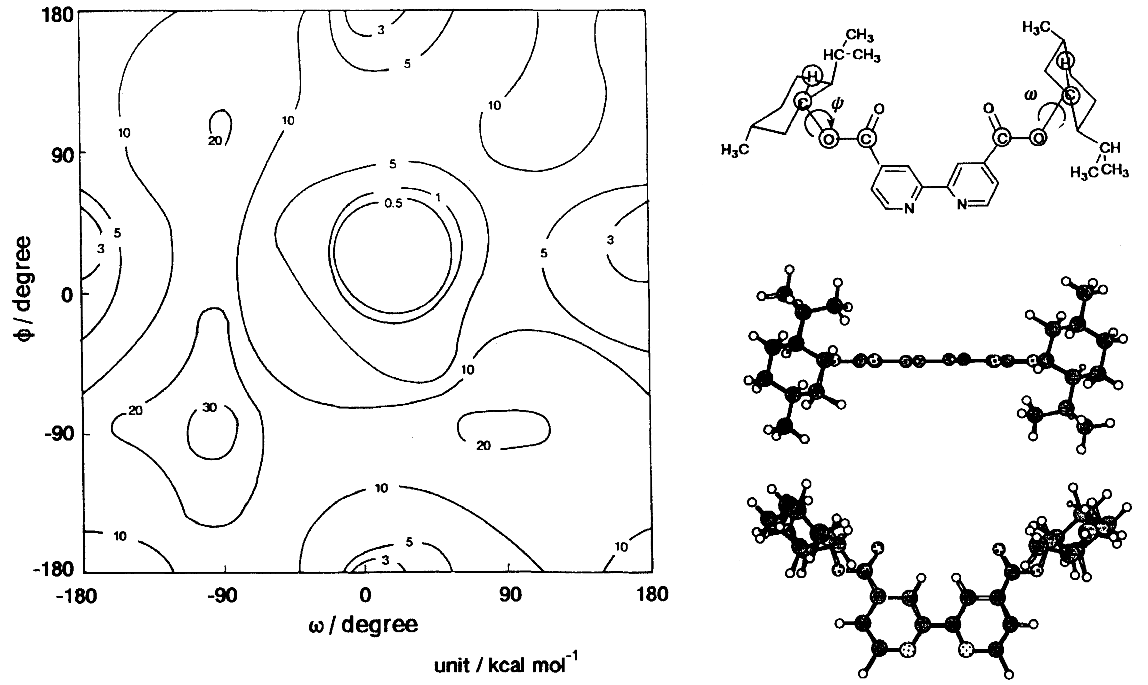
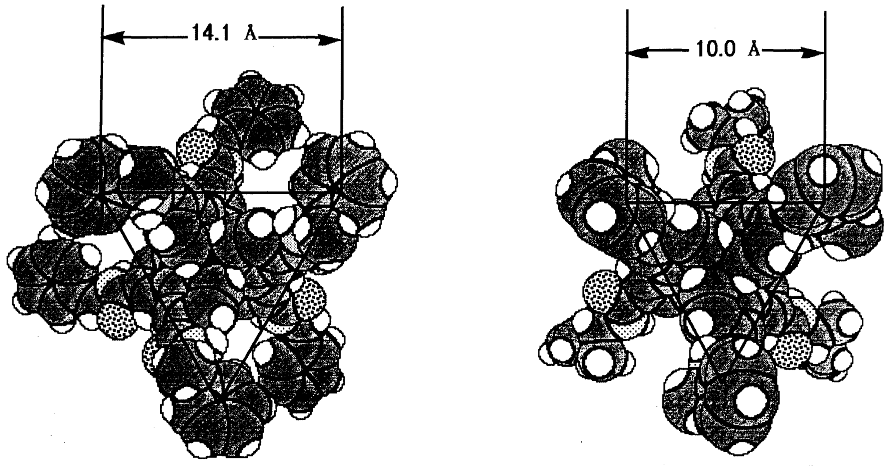


Fig. 6. Contour map of the strain energies of Menbpy as a function of the chiral group about the O–C(menthyl) bonds (ψ and ω) and the most stable structure ((ψ, ω)=(30, 30)).



Δ-[Ru(R-PhEtbpy)$_3$]$^{2+}$

Λ-[Ru(R-PhEtbpy)$_3$]$^{2+}$

Fig. 7. Plausible structures of Δ and Λ-[Ru(R-PhEtbpy)$_3$]$^{2+}$.

of Δ-[Co(acac)$_3$].[2b)] To the contrary it has been reported by Porter et al. that Δ-[Ru(bpy)$_3$]$^{2+}$ reduced Λ-[Co(acac)$_3$] enantioselectively under photoirradiation.[1a)] The origin of the enantioselectivity for Δ-[Ru(R-PhEtbpy)$_3$]$^{2+}$ and the difference between the complex and Δ-[Ru(bpy)$_3$]$^{2+}$ can be related in terms of the conformation of the complex. [Ru{R(or S)-PhEtbpy}$_3$]$^{2+}$ has space between three phenyl rings when viewed along the C$_3$ axes. These phenyl rings form a Λ-configuration around the space in Δ-[Ru(R-PhEtbpy)$_3$]$^{2+}$ in contrast with the metal complex configuration which is formed by 2,2′-bipyridine ligand. Therefore Δ-[Co(acac)$_3$] can fit easier into the space consisting these phenyl rings than the Λ-cobalt complex.

The CD spectrum exhibited that [Ru(Menbpy)$_3$]$^{2+}$ was racemic for molecular asymmetry such as Δ or Λ though there were some asymmetric carbons in the ligand.[2b)] When viewed the stable conformation of the Menbpy ligand obtained by MM calculations from the metal position of the complex on the bipyridine plane, the volume above the plane of the menthyl group was almost same as below the plane, as depicted in Fig. 6. This finding indicates that [Ru(Menbpy)$_3$]$^{2+}$ is racemic for molecular asymmetry. The rotational barriers between the stable conformations in Menbpy are low, therefore the menthyl groups may rotate in the ruthenium complex.

In conclusion, we searched the stable and plausible conformation of the two chiral ligands, (R)-PhEtbpy and ($1R,2S,5R$)-Menbpy with the molecular mechanics calculations. R(or S)-PhEtbpy was shown to have a high barrier in the rotation of chiral groups for the N(amide)–C_α bond, and the phenyl ring of the chiral group were suggested to play an important role for both the molecular asymmetry of the ruthenium complex and the enantioselectivity of the photo-induced reduction of $[Co(acac)_3]$. ($1R,2S,5R$)-Menbpy was shown to have a relatively low barrier for rotation of the chiral group which was probably due to the ester bond. The analyses which combine molecular mechanics calculations and ^{1}H NMR spectrum, as described in this paper, are generally effective for such organic compounds having the same two groups in a molecule, because the NMR signals of these same groups cannot be distinguished.

We thank an allotment of computer time from the Data Processing Center at Kumamoto University. 400 MHz ^{1}H NMR experiments were carried out at Faculty of Pharmacy, Kumamoto University.

References

1) a) G. B. Porter and R. H. Sparks, *J. Chem. Soc., Chem. Commun.*, **1979**, 1094; b) G. B. Porter and R. H. Sparks, *J. Photochem.*, **13**, 123 (1980); c) R. C. Young, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **98**, 286 (1976); d) Y. Kaizu, T. Mori, and H. Kobayashi, *J. Phys. Chem.*, **89**, 332 (1985); e) I. I. Creaser, L. R. Gahan, R. J. Geue, A. Launikonis, P. A. Lay, J. D. Lydon, M. D. McCarthy, A. W. -H. Mau, A. M. Sargeson, and W. H. Sasse, *Inorg. Chem.*, **24**, 2671 (1985); f) D. H. Metcalf, S. W. Snyder, S. Wu, G. L. Hilmes, J. P. Riehl, J. N. Demas, and F. S. Richardson, *J. Am. Chem. Soc.*, **111**, 3082 (1989); g) D. H. Metcalf, S. W. Snyder, J. N. Demas, and F. S. Richardson, *J. Am. Chem. Soc.*, **112**, 5681 (1990).

2) a) K. Ohkubo, T. Hamada, T. Inaoka, and H. Ishida, *Inorg. Chem.*, **28**, 2021 (1989); b) K. Ohkubo, H. Ishida, T. Hamada, and T. Inaoka, *Chem. Lett.*, **1989**, 1545.

3) B. Grossman and R. G. Wilkins, *J. Am. Chem. Soc.*, **89**, 4230 (1967); J. H. Sutter and J. B. Hunt, *J. Am. Chem. Soc.*, **91**, 3107 (1969); N. A. P. Kane-Maguire, R. M. Tollison, and D. E. Richardson, *Inorg. Chem.*, **15**, 499 (1976); E. L. Blinn and R. G. Wilkins, *Inorg, Chem.*, **15**, 2952 (1976); D. A. Geselowitz and H. Taube, *J. Am. Chem. Soc.*, **102**, 4525 (1980); D. A. Geselowitz and H. Taube, *Inorg. Chem.*, **20**, 4036 (1981); S. Kondo, Y. Sasaki, and K. Saito, *Inorg. Chem.*, **20**, 429 (1981); A. G. Lappin, M. C. W. Laranjeira, and R. D. Peacock, *Inorg. Chem.*, **22**, 786 (1983); I. I. Creaser, A. M. Sargeson, and A. W. Zanella, *Inorg. Chem.*, **22**, 4022 (1983); D. P. Martone, P. Osvath, and C. Eigenbrot, *Inorg. Chem.*, **24**, 4693 (1985); Y. Sasaki, K. Meguro, and K. Saito, *Inorg. Chem.*, **25**, 2277 (1986); A. G. Lappin, R. A. Marusak, and P. Osvath, *Inorg. Chem.*, **26**, 4292 (1987); D. A. Geselowitz, A. Hammershøi, and H. Taube, *Inorg. Chem.*, **26**, 1842 (1987); P. Osvath and A. G. Lappin, *Inorg. Chem.*, **26**, 195 (1987); R. A. Marusak, P. Osvath, M. Kemper, and A. G. Lappin, *Inorg. Chem.*, **28**, 1542 (1989); A. Tatehata and T. Mitani, *Chem. Lett.*, **1980**, 1167; R. M. L. Warren, A. G. Lappin, B. D. Mehta, and H. M. Neumann, *Inorg. Chem.*, **29**, 4185 (1990).

4) A. J. Hopfinger and R. A. Pearlstein, *J. Comput. Chem.*, **5**, 486 (1984).

5) MM2PRIME for Hitac, JCPE, P011; the program was written by Eiji Osawa, Carlos Jaime, Teruyo Fujiyoshi, Hitoshi Goto, and Keisuke Imai. It was revised for FACOM by Kimiharu Matsuzaki in our group, Kumamoto University.

6) MOPAC ver. 6 by J. J. P. Stewart, JCPE, P044; Revised by Yoshihisa Inoue for FACOM.

7) J. S. Binkley, M. Frisch, K. Reghavachari, D. DeFrees, H. B. Schlegel, R. Whiteside, E. Fluder, R. Seeger, and J. A. Pople, "Carnegie-Mellon Quantum Chemistry Archive," Carnegie-Mellon University, Pittsburgh, PA (1983).

8) a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); b) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963); c) A. Pardi, M. Billeter, and K. Wutherich, *J. Mol. Biol.*, **180**, 741 (1984).

9) D. P. Rillema, D. S. Jones, and H. A. Levy, *J. Chem. Soc., Chem. Commun.*, **1979**, 849; M. H. Chisholm, J. A. Connor, J. C. Huffman, E. M. Kober, and C. Overton, *Inorg. Chem.*, **23**, 2298 (1984).