Theoretical Study of a Conformational Change Occurring with Lithium Complexation to a Tetra-aza Macrocycle Containing 2,2′-Bipyridines

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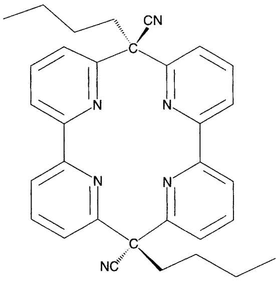
Ab initio Hartree–Fock theory was used to determine the structures of model molecules of a dibutyl dicyano tetra-aza macrocycle (**1**) containing 2,2′-bipyridines and their lithium complexes. Energy profiles for the conformational inversion, which is closely related to the complexation process of a lithium cation, were also studied. Macrocycles having cyano groups on the bridge methylene carbons were found to be good macrocyclic models related to the macrocycle (**1**). The energy profiles of stationary points and the vibrational frequencies of macrocycles and their lithium complexes reveal that conformational inversion in the lithium complexes is plausible after lithium complexation. The difference in the vibrational frequencies corresponding to the movement of the lithium cation suggests that C_{2v}-like skeletons in the macrocyclic moiety have a stronger interaction between the lithium cation and coordinating nitrogens than the C_{2h} structure.

Macrocyclic molecules have been of much interest for numerous potential applications, such as the design of novel functional molecules. The ability as chemically selective sensors is one of the fascinating properties of macrocyclic conjugated systems with pyridyl-based ligands.[1] The coordination of metal ions may lead to conformational, optical, or electrochemical changes in the conjugated system, such as aza-macrocycles and crown ethers. Feller et al. reported on a theoretical investigation of complexation to crown ethers.[2] We previously synthesized several new macrocycles with pyridyl-based ligands that show chemically fascinating properties.[3,4] We have reported that a dibutyl dicyano tetra-aza macrocycle (**1**) containing four pyridine rings having *cis*- and *trans*-isomers possesses the ability to bind to a lithium cation (Chart 1).[3] Stability constants reveal that the *cis*-isomer of the macrocycle (**1**) has a higher complexation ability toward the lithium cation than the *trans*-isomer. The *trans*-isomer of the macrocycle (**1**) has another fascinating property, that is, a great fluorescence enhancement (over 1100 fold) in response to complexation with the lithium cation.[4] We previously suggested, based on quantum chemical calculations, that one of the reasons for the fluorescence enhancement of the lithium complex is weak fluorescence due to intersystem crossing in the *trans*-isomer of the metal-free macrocycle.[5] Another possible explanation is the flexibility of the metal-free macrocyclic molecule, which could cause energy loss due to the molecular vibrations. The vibrational properties and conformational inversion of the macrocyclic moiety are therefore worth discussing.

The ^{1}H NMR chemical shifts of two isomers of macrocycle (**1**) and their lithium complexes were reported.[3b] The temperature-dependent ^{1}H NMR spectrum of the lithium complex of *trans*-isomer of macrocycle (**1**) strongly supported a square-pyramidal unsymmetrical structure. It contains the signal due to the α-methylene protons of the butyl groups, which corresponds to one peak above −10 °C, and was split below −40 °C. Two different types of methylene protons were observed at low temperatures, under which conditions a conformational inversion of the lithium complex was sufficiently slow and the unsymmetrical square-pyramidal structure was fixed. It is also evidence that the conformational inversion occurs at higher temperature above −10 °C in the lithium complex. No split was observed in the case of the metal-free *trans*-isomer and the lithium complex of the *cis*-isomer, even below −60 °C. These two species had been found to have local minimum structures with C_i and C_2 symmetries, respectively, based on ab initio MO calculations.[5] Whether the conformational inversion occurs or not, the α-methylene H atoms are equivalent to each other due to the symmetry. This may be the reason why no split of the ^{1}H NMR signal was observed at a lower temperature. In other words, no split does not mean that they have no conformational inversions, but that a conformational change cannot be detected using the temperature-dependent ^{1}H NMR spectrum for the above-mentioned two cases. The purpose of this study was to elucidate the difference in the vibrational properties and the conformational inversion of the macrocyclic moiety among the *cis*/*trans* isomers and their lithium complexes.

In this paper, we report on an ab initio molecular orbital (MO) study of two types of model molecules other than the dibutyl dicyano tetra-aza macrocycle (**1**), itself, and its lithium complex. In order to focus on a conformational change of the macrocyclic moiety and to reduce the computational costs, a macrocycle (**2**) having no butyl and cyano groups on the bridge methylene carbons, and another (**3**) having two cyano groups



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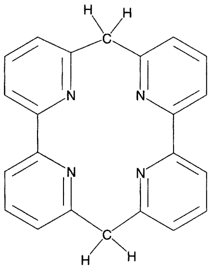

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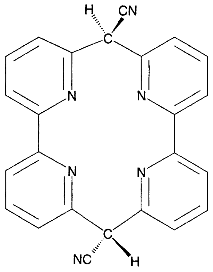

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Chart 1.

along with the resulting *cis*/*trans* isomers were chosen for our calculations. The effect of alkyl groups is not discussed in this paper, since macrocycle (**3**) was found to be a good enough model for macrocycle (**1**), as described below. In addition to the optimized geometries, we discuss the energy profiles for the conformational inversions and the vibrational features of the macrocyclic moieties.

Computational Details

Geometry optimizations of macrocycles (**2**) and (**3**) at the RHF/3-21G[6] level of theory were carried out using the GAMESS program.[7] The 6-31G* basis[8] was also selected for geometry optimizations of macrocycle (**2**) to examine the size effects of the basis sets. Force-constant matrices (hessians) at the RHF/3-21G level were calculated at stationary points in order to identify them as minima (all positive constants), transition states (one negative force constant), or higher-order saddle points. WinMOPAC[9] and MacMolPlt[10] in GAMESS were used to visualize the structures and vibrational modes, respectively. The computers used were an SGI Origin 2000 and IBM RS/6000s at Ochanomizu University and an SGI Origin 2000 and an IBM SP2 system at the computer center in IMS (Institute of Molecular Science), Okazaki.

Results and Discussion

Optimized Geometries of Macrocycle (2) and its Lithium Complex. Geometry optimizations of the macrocycle (**2**) were carried out under constraint with D_{2h} symmetry at the RHF/3-21G level. The optimized structure is shown in Fig. 1. Its four pyridine rings are coplanar, because it has D_{2h} symmetry. Hessian calculations for this stationary point have revealed that the structure has three imaginary frequencies, indicating that it is a third-order saddle point. Geometry searches along the three vibrational modes of the imaginary frequencies lead

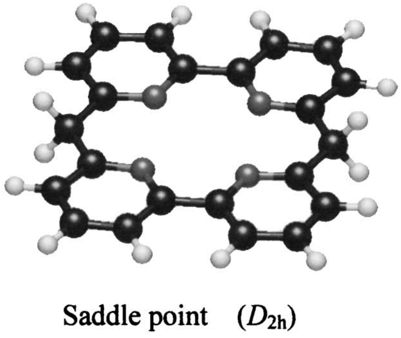


Fig. 1. Optimized structure of the macrocycle (**2**) under constraint with D_{2h} symmetry at the RHF/3-21G level. The D_{2h} structure has three vibrational modes of imaginary frequencies.

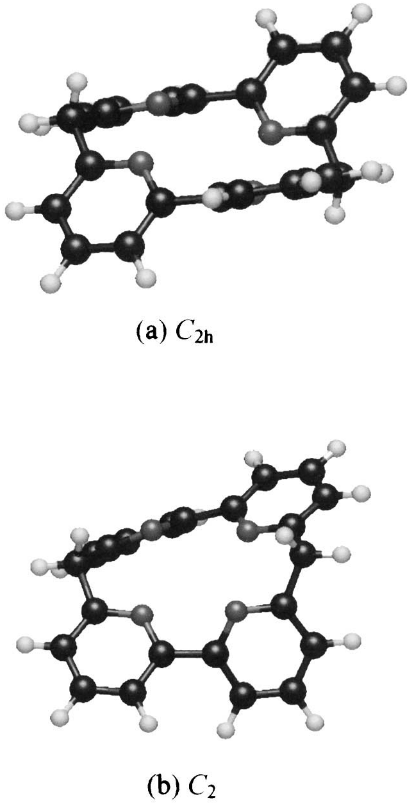
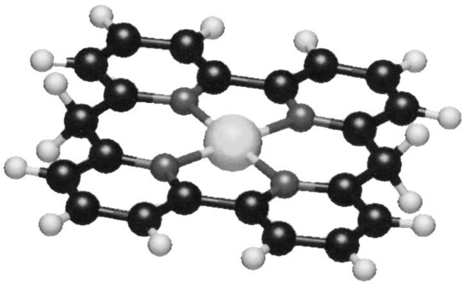
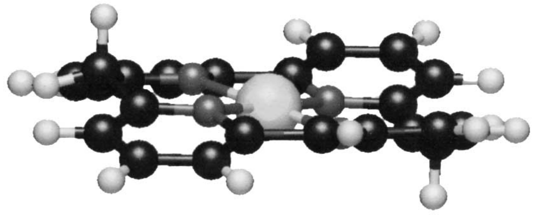


Fig. 2. Structures of energy local minima of macrocycle (**2**) at the RHF/3-21G level with C_{2h} (a) and C_2 (b) symmetries.

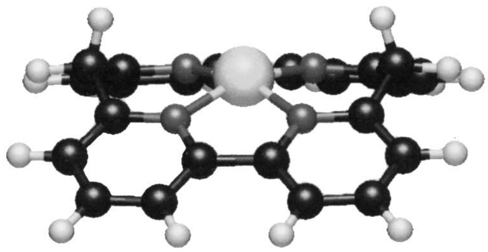


Saddle point (D_{2h})

Fig. 3. Optimized structure of the lithium cation complex of macrocycle (**2**) under constraint with D_{2h} symmetry at the RHF/3-21G level. The D_{2h} structure has three vibrational modes of imaginary frequencies.



(a) C_{2h}



(b) C_{2v}

Fig. 4. Structures of energy local minima of lithium cation complexes of macrocycle (**2**) at the RHF/3-21G level with C_{2h} (a) and C_{2v} (b) symmetries.

to C_{2h}, C_2, and D_2 structures of lower symmetries. The first two structures are shown in Figs. 2a and 2b. The hessian calculations identified both structures as local minima. The C_{2h} structure (Fig. 2a) is similar to that of the *trans*-isomer of macrocycle (**1**) having the twisting two pyridine rings in the bipyridine moiety, while the C_2 structure (Fig. 2b) is similar to that of the *cis*-isomer, in which the lone pairs of four pyridine nitrogens point in the same direction.[3b,5] The D_2 structure was found by hessian calculations to have two vibrational modes with imaginary frequencies. Further geometry searches along these two vibrational modes led to the discovery of another two structures with C_2 symmetry. These two C_2 structures are not discussed in detail in this paper, because they are less stable than the C_{2h} and C_2 structures described above

Selected optimized geometric parameters of the local minimum structures with C_{2h} and C_2 symmetries of macrocycle (**2**) are listed in Table 1 along with those of the third-order saddle point with D_{2h} symmetry. The geometric features of each pyridine ring are similar, independent of the symmetry. Each pyridine ring has a planar sub-structure, with similar bond distances among the three (C_{2h}, C_2, and D_{2h} symmetries), though the data are not shown in this paper.

It is important to identify the key parameters which determine the geometries and the conformation of the macrocycles. To allow for a comparison of the sizes of the macrocycle cavities, the distances between N2′ and N2″ are given in Table 1. There is little difference in the distances among the three stationary points (C_{2h}, C_2, and D_{2h}). The bond angles for C3–C7–C3″ and N2–C3–C7 of the two local minimum structures of C_{2h} and C_2 symmetries are similar, but differ from the third-order saddle point of D_{2h} symmetry. The dihedral angles between the two pyridine rings in the bipyridine moiety are 55.0(C_{2h}), 32.7(C_2), and 0.0(D_{2h}) degrees. The D_{2h} structure is planar, i.e., the dihedral angle is 0.0 degree due to the symmetry restriction. The planar structure of D_{2h} symmetry is less stable because of repulsive lone-pair electrons on the four nitrogen atoms. In contrast, structures having twisted pyridine rings are more stable for C_{2h} and C_2 symmetries.

The stationary point with D_{2h} symmetry for the lithium complex of macrocycle (**2**) as well as for the metal-free macrocycle (**2**) was found by hessian calculations to have three imaginary frequencies. These two D_{2h} structures are quite similar

Table 1. Selected Optimized Geometric Parameters of Local Minimum Structures (C_{2h} and C_2) and the Third-Order Saddle Point (D_{2h}) of Macrocycle (**2**) at the RHF/3-21G Level

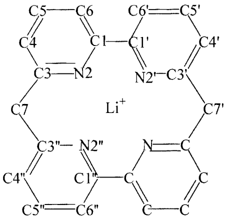
Symmetry	C_{2h}	C_2	D_{2h}
N2′–N2″/Å	4.053 (4.058)	3.872, 4.048 (3.862, 4.068)	3.946 (3.931)
Cl–Cl′/Å	1.489 (1.500)	1.488 (1.499)	1.493 (1.504)
C3–C7/Å	1.520 (1.522)	1.514, 1.526 (1.516, 1.527)	1.522 (1.523)
C3–C7–C3″/°	112.9 (114.0)	111.6 (113.7)	122.7 (123.9)
N2–C3–C7/°	116.8 (116.4)	116.6, 116.6 (116.8, 116.2)	123.1 (122.1)
N2–Cl–Cl′–N2′/°	55.0 (56.2)	32.7 (38.9)	0.0 (0.0)

Values in parentheses are optimized geometric parameters at the RHF/6-31G* level.

Table 2. Selected Optimized Geometric Parameters of Local Minimum Structures (C_{2h} and C_2) and the Third-Order Saddle Point (D_{2h}) of the Lithium Complexes of Macrocycle (**2**) at the RHF/3-21G Level

Symmetry	C_{2h}	C_{2v}	D_{2h}
Li–N2/Å	1.982 (1.989)	1.996 (2.020)	1.981 (1.983)
N2′–N2″/Å	3.963 (3.977)	3.915 (3.932)	3.962 (3.966)
C1–C1′/Å	1.489 (1.500)	1.492 (1.503)	1.490 (1.501)
C3–C7/Å	1.521 (1.523)	1.521 (1.522)	1.522 (1.523)
C3–C7–C3″/°	120.2 (120.8)	114.4 (115.7)	123.5 (124.8)
N2–C3–C7/°	120.2 (119.2)	117.8 (117.3)	123.7 (122.8)
N2–C1–C1′–N2′/°	23.3 (26.6)	0.0 (0.0)	0.0 (0.0)

Values in parentheses are optimized geometric parameters at the RHF/6-31G* level.



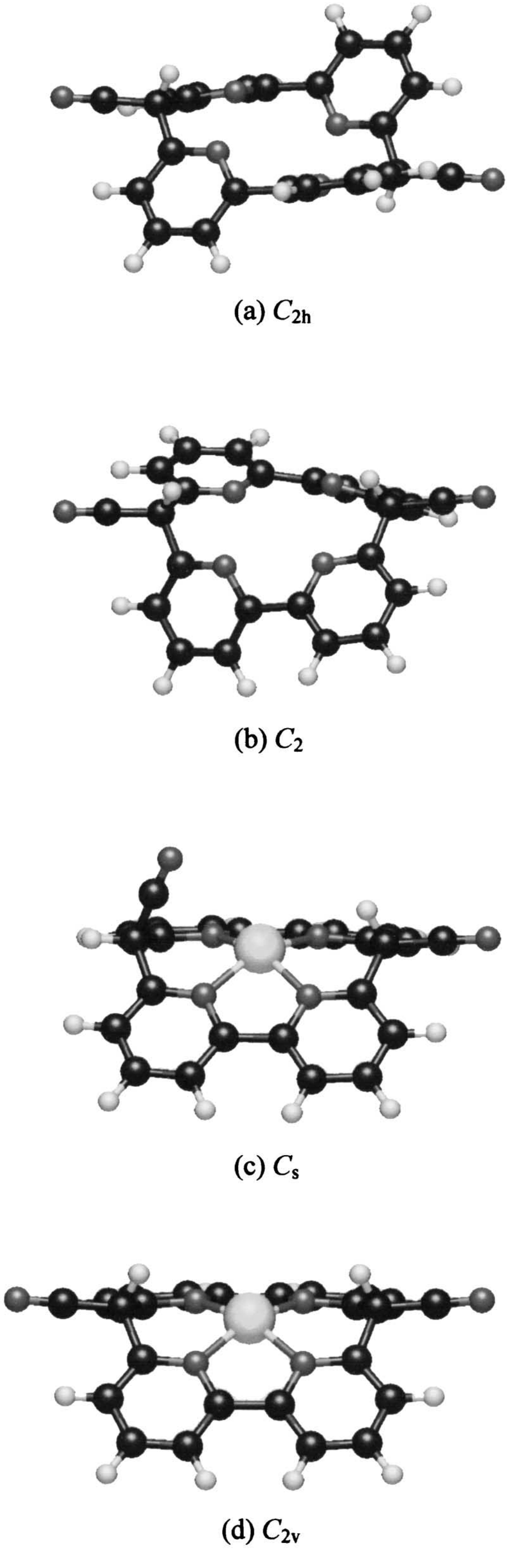
(see Figs. 1 and 3). A geometry search for local minimum structures of lithium complexes of C_{2h} and C_{2v} symmetries was successful. The obtained C_{2h} and C_{2v} structures are shown in Fig. 4. The C_{2v} structure is more stable than the C_{2h} structure. This C_{2v} structure of the lithium complex shown in Fig. 4b is similar to that of the metal-free macrocycle (**2**) with C_2 symmetry shown in Fig. 2b, except for dihedral angles in the bipyridine moiety. Because two pyridines in the bipyridine moiety in the C_{2v} structure are coplanar due to a symmetry restriction, a lithium cation coordinated by four nitrogen atoms is placed over the cavity. In contrast, the cationic lithium complex of C_{2h} symmetry has a lithium cation in the center of the cavity. The structure of the macrocyclic moiety in the complex of C_{2h} symmetry is similar to the D_{2h} structure of the lithium complex, which is the third-order saddle point, as shown in Fig. 3.

Selected optimized geometric parameters of the local minimum structures with C_{2h} and C_2 symmetries of lithium complexes of macrocycle (**2**) are listed in Table 2 along with those of the third-order saddle point with D_{2h} symmetry. It was found that the bond angles for C3–C7–C3″ and N2–C3–C7 increase to a greater or lesser extent upon complexation with a lithium cation (see Tables 1 and 2). The C_{2v} and D_{2h} structures have planar bipyridine moieties, i.e., a dihedral angle of 0.0 degree due to a symmetry restriction. The C_{2h} structure has a smaller dihedral angle (23.3 degrees) than that of metal-free macrocycle (55.0 degrees) due to the lithium-nitrogen bond.

Geometry optimizations at the RHF/6-31G* level of theory were also carried out to check the basis set dependency, especially with regard to the effects of the polarization functions. The optimized geometric parameters are listed in parentheses in Tables 1 and 2. Both the RHF/3-21G and RHF/6-31G* levels of theory give the same trend, with the maximum differences in bond lengths and angles being 0.024 Å and 2.1 degrees, respectively. It was thus found that the basis set dependency is not as large in these cases. Among the geometric parameters listed in Table 1, only the dihedral angle of N2–C1–C1′–N2′ for C_2 symmetry remarkably depends on the basis sets used. This angle was estimated to be 32.7 and 38.9 degrees, respectively, using 3-21G and 6-31G* basis sets.

Geometric Features of Dicyano Macrocycle (3) and its Lithium Complex. The energy global minimum structures of *trans*- and *cis*-isomers of the dicyano macrocycle (**3**) and its lithium complexes are shown in Fig. 5. Both isomers have cyano groups parallel to the bridge bonds across the two pyridine rings. This geometric feature indicates that repulsive interactions among the lone-pair electrons on nitrogen atoms are prevented for cyano groups and bipyridine moieties. The structures of these isomers of the dicyano macrocycle (**3**), shown in Figs. 5a and 5b, are, respectively, similar to the energy-minimum structures of the *trans*- and *cis*-isomers of macrocycle (**1**).[5] Lithium complexes of the *trans*- (C_s, Fig. 5c) and *cis*-isomers (C_{2v}, Fig. 5d) of macrocycle (**3**) have geometric features similar to those of the lithium complexes of macrocycle (**2**) (C_{2v}, Fig. 4b) and macrocycle (**1**).[5] It is noteworthy that the feature of geometric change upon complexation of the *trans*- and *cis*-isomers of macrocycle (**3**) is quite similar to the case of macrocycle (**1**). *trans*-Isomers have drastic conformational changes in their macrocyclic moiety (see Figs. 5a and 5c), while *cis*-isomers of the metal-free macrocycle and its lithium complex have only slight differences (see Figs. 5b and 5d). The other local minima with C_1 and C_s, respectively, for the *trans*- and *cis*-isomers of the macrocycle (**3**) were found to be less stable, as well as those with C_{2h} and C_s, respectively, for the *trans*- and *cis*-isomers of its lithium complex. They are not described in detail in this paper, except for the C_{2h} structure of the *trans*-isomer of the lithium complex, which are mentioned in the following section.

The geometric parameters of the global minimum structures of macrocycle (**3**) are listed in Table 3. The cyano groups in macrocycle (**3**) affect the geometric parameters, except for the bond distances (see Tables 1 and 3). As for the bond angles, the *trans*-isomer of macrocycle (**3**) has smaller bond angles by 2 degrees for C3–C7–C3″ and N2–C3–C7 than the C_{2h} structure of macrocycle (**2**). This is also the case for the *cis*-isomer



(a) C_{2h}

(b) C_2

(c) C_s

(d) C_{2v}

Fig. 5. Structures of energy global minima of *cis*/*trans*-isomers of macrocycle (**3**) and their lithium cation complexes at the RHF/3-21G level : *trans*-isomer (C_{2h}) (a), *cis*-isomer (C_2) (b), and lithium complex of *trans*-isomer (C_s) (c), lithium complex of *cis*-isomer (C_{2v}) (d).

Table 3. Selected Optimized Geometric Parameters for the *trans*-Isomer (C_{2h}) and *cis*-Isomer (C_2) of Macrocycle (**3**) at the RHF/3-21G Level

	trans-Isomer (C_{2h})	*cis*-Isomer (C_2)
N2′–N2″/Å	4.086	4.017, 3.878
Cl–Cl′/Å	1.489	1.488
C3–C7/Å	1.534	1.539, 1.528
C3–C7–C3″/°	110.9 [109.9]	109.8 [108.2]
N2–C3–C7/°	114.3	114.5, 113.9
N2–Cl–Cl′–N2′/°	61.4 [60.1]	27.3 [22.3]

Values in square brackets are the geometric parameters of the *trans*-isomer (C_i) and *cis*-isomer (C_2) of macrocycle (**1**).

Table 4. Selected Optimized Geometric Parameters for Lithium Complexes of *trans*- and *cis*-Isomers of Macrocycle (**3**) at the RHF/3-21G Level

	Lithium complex of *trans*-isomer (C_s)	Lithium complex of *cis*-isomer (C_{2v})
Li–N2/Å	2.020, 2.010	1.966
N2′–N2″/Å	3.894	3.903
Cl–Cl′/Å	1.491	1.492
C3–C7/Å	1.536, 1.531	1.536
C3–C7–C3″/°	111.5, 112.0	112.1
	[107.6, 110.4]	[111.7]
N2–C3–C7/°	115.3, 116.0	115.3
N2–Cl–Cl′–N2′/°	1.6 [−1.4, 5.4]	0.0 [1.0]

Values in square brackets are the geometric parameters for lithium complexes of the *trans*-isomer (C_1) and *cis*-isomer (C_2) of macrocycle (**1**).

of macrocycle (**3**) with C_2 symmetry and another local minimum with C_2 symmetry of macrocycle (**2**). The difference in the dihedral angles among macrocycles (**2**) and (**3**) is 5–7 degrees. The C3–C7–C3″ angle and the dihedral angle for the N2–C1–C1′–N2′ of macrocycle (**3**) are in better agreement with the geometric parameters of macrocycle (**1**) (see the values in square brackets in Table 3) than are those of macrocycle (**2**). In addition to the conformational features of the energy global minima of the *trans*- and *cis*-isomers of macrocycle (**3**), these described geometric parameters also suggest that macrocycle (**3**) with two cyano groups on the bridge carbon is more acceptable as a model for macrocycle (**1**) than is macrocycle (**2**) having no cyano groups.

The lithium complex of macrocycle (**3**) is also a good model for the lithium complex of macrocycle (**1**). The geometric parameters not only for bond distances, but also for angles are very close to those of macrocycle (**1**). For example, the differences between the C3–C7–C3″ angle and the N2–C1–C1′–N2′ dihedral angle for the lithium complex of the *trans*-isomer (C_s) of macrocycle (**3**) and that of the *trans*-isomer (C_1) of macrocycle (**1**) were estimated to be, respectively, 2–4 degrees and 0–4 degrees, as shown in Table 4. As for between the C_{2v} structure of the lithium complex of macrocycle (**2**) and the *trans*-isomer (C_1) of macrocycle (**1**), the difference in the C3–C7–C3″ angle was estimated to be 4–7 degrees. The effect of cyano groups on the geometric parameters in lithium complexes is similar to that in the metal-free isomers described above.

More specifically, all of the geometric parameters, except for the C1–C1′ bond distance, are affected.

Energy Profiles Accompanying the Conformational Inversion. We previously studied the geometric features of macrocycle (**1**).[5] The *cis*-isomer of macrocycle (**1**) and its lithium complex have macrocyclic moieties with similar conformational structures. In other words, the *cis*-isomer of macrocycle (**1**) does not change much conformationally upon complexation with a lithium cation. In contrast, the conformational structures between the *trans*-isomer of macrocycle (**1**) and its lithium complex differ greatly. Such a conformational change may be one of the reasons for the difference in complexation ability, because the *cis*-isomer complexes with lithium much more easily than does the *trans*-isomer.[11] We attempted in the present study to examine the conformational features and energetics along with the complexation of the lithium cation. However, it was difficult to follow the reaction path because of the flexibility of the large butyl groups, the complicated geometries of the macrocyclic moiety, and the computational costs. Instead of reaction barrier heights for lithium complexation, the energies of conformational inversions of the macrocyclic moiety were compared between the macrocycle and its lithium complex to estimate which has the smaller energy barrier of macrocyclic inversion related to lithium complexation. Macrocycle (**3**) was studied as a model system for macrocycle (**1**) because its features are quite similar to those of macrocycle (**1**), as discussed in the previous section. Macrocycle (**2**) was also studied for cases in which the structures and energies could not be obtained for macrocycle (**3**), e.g., for the TS of inversion with D_{2h} symmetry, which only macrocycle (**2**) has. Energy profiles of stationary points for macrocycles (**2**) and (**3**) are shown in Fig. 6a, in which the energies of the corresponding C_{2h} structures are, respectively, references for macrocycles (**2**) and (**3**). The D_{2h} structure of macrocycle (**2**) is the third-order saddle point, not the transition state between the two local minima (C_{2h} and C_{2v}-like structures) that are connected by the inversion of the macrocyclic moiety. The real energy barriers of conformational inversion must be lower than those estimated using the third-order saddle point. However, the relative tendencies between metal-free macrocycles and their lithium complexes can be extracted from the estimated values (Fig. 6). Using the D_{2h} energy of macrocycle (**2**) for estimating the energy barrier height for the conformational inversion of the macrocyclic moiety, the energy of inversion was estimated to be 12.70 and 13.72 kcal mol^{-1}, respectively, with 3-21G and 6-31G* basis sets, at the RHF levels of theory. To compare this value with that of its lithium complex, the relative energies for lithium complexes were plotted, as shown in Fig. 6b.[12] The estimated values for the energy barrier height of the lithium complex are 2.44 and 3.52 kcal mol^{-1}, respectively, with 3-21G and 6-31G* basis sets, at the RHF levels of theory.[13] It was found that the energy barriers of inversion for lithium complexes are much lower than those for metal-free macrocycles. These results indicate that a conformational inversion in the lithium complexes is plausible after lithium complexation, as shown in Fig. 7.[14]

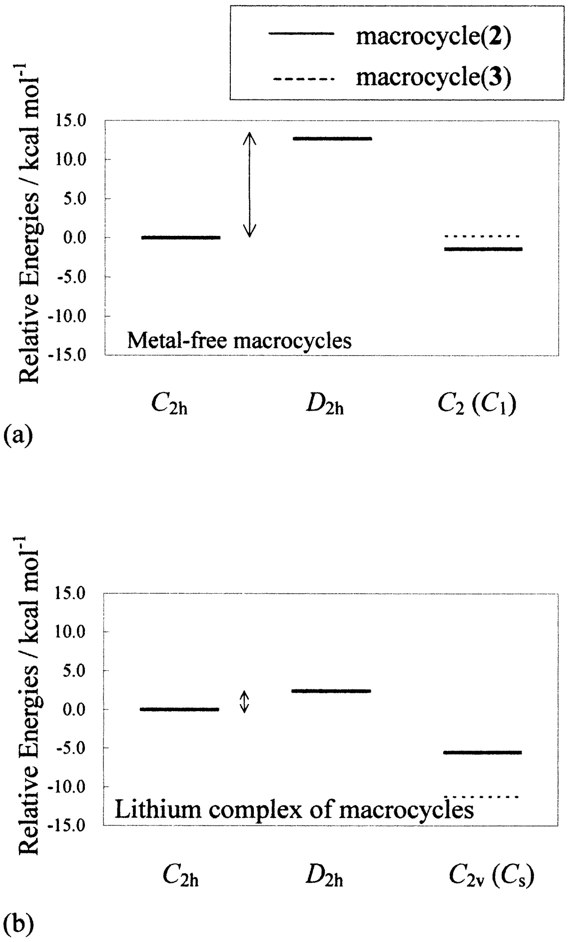


Fig. 6. (a) Energy profiles of stationary points for macrocycle (**2**) and the *trans*-isomer of macrocycle (**3**). Relative energies compared to those of the C_{2h} structures are shown in kcal mol^{-1} calculated at the RHF/3-21G level. Relative energies of metal-free macrocycle (**2**) for the D_{2h} saddle point (center) and the C_2 local minimum (right) are drawn as straight lines. Those of the *trans*-isomer of macrocycle (**3**), which has C_1 symmetry with a C_2-like skeleton in the macrocyclic moiety, are indicated as a dashed line.
(b) Energy profiles of stationary points for the lithium complexes of both macrocycle (**2**) and the *trans*-isomer of macrocycle (**3**). Relative energies compared to those of the C_{2h} structures are shown in kcal mol^{-1} calculated at the RHF/3-21G level. Relative energies of the lithium complexes of macrocycle (**2**) for the D_{2h} saddle point (center) and the C_{2v} local minimum (right) are drawn as straight lines. Those of the lithium complex of *trans*-isomer of macrocycle (**3**), which has C_s symmetry with a C_{2v}-like skeleton of macrocyclic moiety, are indicated as a dashed line.

Vibrational Modes for Macrocycles (2) and (3) and Their Lithium Complexes. Hessian calculations were carried out to identify the stationary points obtained by geometry optimizations as minima (all positive constants), transition states (one negative force constants), or higher-order stationary points. Nicholas et al. reported low-lying vibrational frequencies corresponding to the motion of the cation in M$^+$–Benzene complexes (M: alkali-metal), to discuss the interaction of the benzene with the cation.[15] The vibrational modes concerning the macrocyclic moiety and the vibrational frequencies obtained in

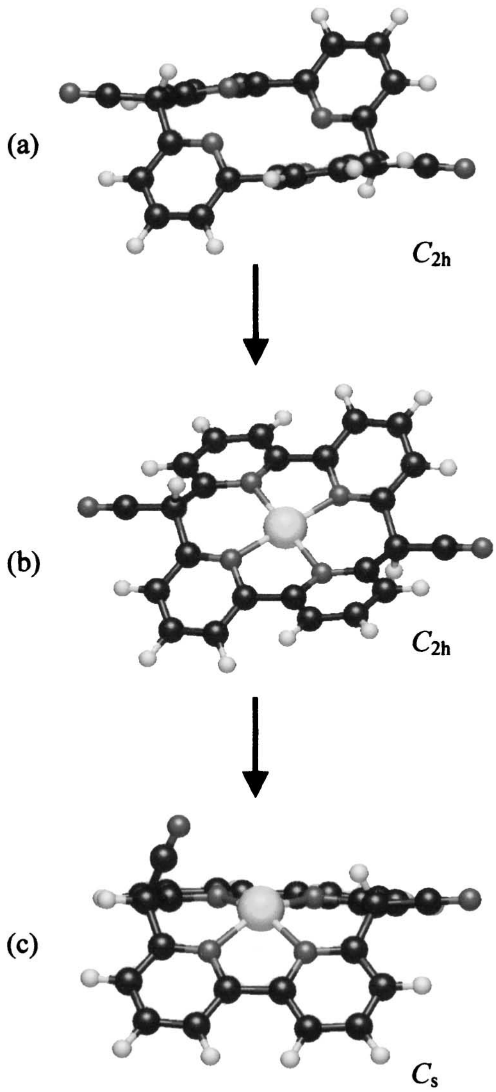


Fig. 7. A plausible conformational inversion of the *trans*-isomer of macrocycle (**3**): metal-free *trans*-isomer (C_{2h}) (a), the lithium complex of *trans*-isomer (C_{2h}) (b), the lithium complex of *trans*-isomer (C_s) (c).

the present study were examined in order to interpret the complexing ability of the lithium cation. There is a B_u mode related to the motion of conformational inversion in the macrocyclic moiety for each of the C_{2h} structures of the macrocycle (**2**) and its lithium complex. Each B_u mode is shown in Fig. 8. In these cases the vibrational modes lead to changes in symmetry from C_{2h} to C_{2v}. The C_{2h} structure of macrocycle (**3**) also has a B_u mode related to the conformational inversion in the macrocyclic moiety, which leads to a change in symmetry from C_{2h} to C_s. Each of these B_u modes has the lowest harmonic vibrational frequency among all of the vibrational modes. The frequencies of the B_u modes for macrocycles (**2**) and (**3**) are compared with those for their lithium complexes in Fig. 9. It is noteworthy that the vibrational frequencies of the lithium complexes of both macrocycles (**2**) and (**3**) are lower than those of the metal-free macrocycles. These lower frequencies are consistent with the plausible conformational inversion in lithium complexes, as discussed below.

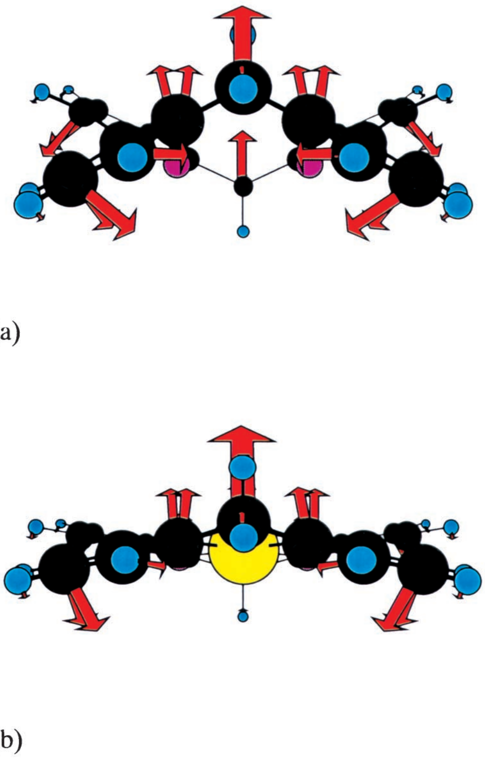


Fig. 8. $1B_u$ vibrational modes for the C_{2h} structure of macrocycle (**2**) (a) and its lithium complex (b) obtained by hessian calculations at the RHF/3-21G level. Arrows indicate the vibrational motion of the molecules.

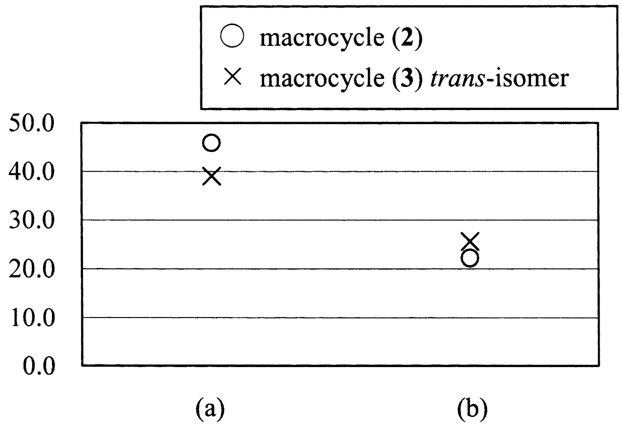


Fig. 9. Comparison of the harmonic vibrational frequencies (cm^{-1}) of the B_u modes for C_{2h} symmetry between metal-free macrocycles (a) and their lithium complexes (b) at the RHF/3-21G level.

Vibrational modes corresponding to the motion of the lithium cation against the macrocyclic moiety were examined to determine the binding properties between the cation and the macrocyclic moiety. Figure 10 shows the B_u mode of the C_{2h} structure and the A_1 mode of the C_{2v} structure for the lithium complex of macrocycle (**2**) as examples. Table 5 lists the vibrational frequencies related to the vibrational modes of the lithium cation leaving the cavity of the macrocycles in a perpendicular direction for lithium complexes with C_{2h} and C_{2v}

Table 5. Vibrational Frequencies (cm^{-1}) Related to the Vibrational Modes of the Lithium Cation Leaving the Cavity of Macrocycles in a Perpendicular Direction for Lithium Complexes with C_{2h} and C_{2v} Structures of Macrocycle (**2**) and with C_{2h} and C_s Structures of the *trans*-Isomer of Macrocycle (**3**)

Macrocycle (**2**)		Macrocycle (**2**)		Macrocycle (**3**)		Macrocycle (**3**)	
C_{2h}		C_{2v}		*trans*-isomer C_{2h}		*trans*-isomer C_s	
B_u	227.6	A_1	301.1	B_u	257.8	A'	309.3
B_u	288.5	A_1	337.2	B_u	281.1	A'	313.4
	—	A_1	360.9		—	A'	333.0
	—		—		—	A'	354.7
	—		—		—	A'	374.0

These frequencies were calculated at the RHF/3-21G level.

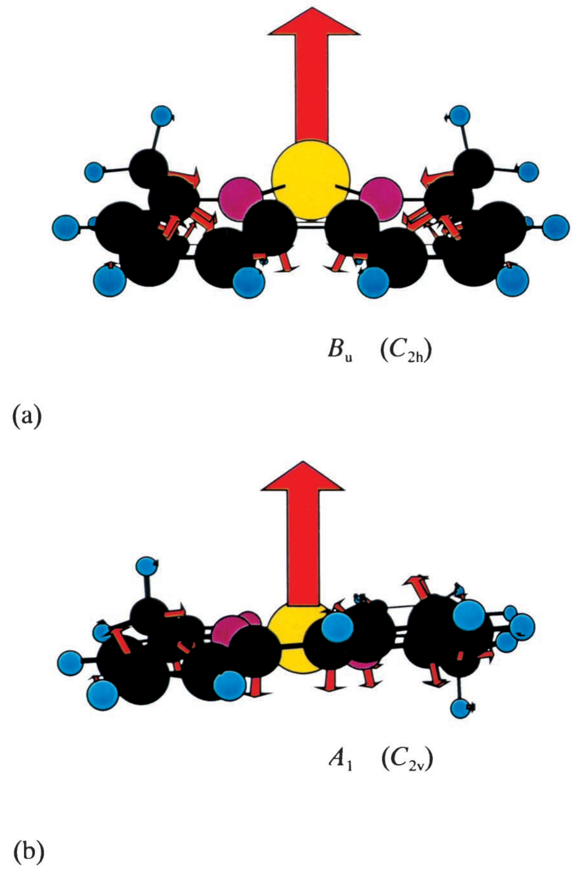


Fig. 10. Vibrational modes corresponding to the motion of the cation in the lithium complex of macrocycle (**2**) at the RHF/3-21G level. Arrows indicate the vibrational motion of the molecules: the B_u mode of C_{2h} symmetry (288.5 cm^{-1}) (a) and the A_1 mode of C_{2v} symmetry (337.2 cm^{-1}) (b).

structures for macrocycle (**2**) and with C_{2h} and C_s structures for the *trans*-isomer of macrocycle (**3**). Due to its low symmetry, the C_s structure has more modes related to the movement of lithium cation than the other structures. It is worthwhile mentioning that the C_{2h} structure has lower frequencies (227–288 cm^{-1}) than the C_{2v} and C_s structures (301–373 cm^{-1}) for both macrocycles (**2**) and (**3**). The C_{2v} and C_s structures have, respectively, coplanar and approximately coplanar pyridine rings in the bipyridine moiety, contrary to the twisted pyridine rings in the C_{2h} structure. The structural distinction of the macrocyclic moiety is the dihedral angles between the two pyridine rings, which is closely related to the difference in the vibrational frequencies. Higher vibrational frequencies for the C_{2v} and C_s structures by 70–80 cm^{-1} than for the C_{2h} structure indicate that C_{2v}-like skeletons in the macrocyclic moiety have a stronger interaction between the lithium cation and coordinating nitrogens than the C_{2h} structure. These results are consistent with the C_{2v}-like skeletons of lithium complexes having greater stability than the C_{2h} structures.

Concluding Remarks

Conformational change of the macrocycles cannot always be detected by such experiments as ^1H NMR spectroscopy, as described in Introduction. In order to focus on this conformational behavior, we carried out geometry optimizations and vibrational analysis of two kinds of model molecules of a dibutyl dicyano tetra-aza macrocycle (**1**) containing two 2,2-bipyridine moieties at the RHF/3-21G level of theory. Macrocycle (**2**), in which butyl and cyano groups are replaced with hydrogen atoms, have local minima with C_{2h} and C_2 symmetries. The lithium complex of macrocycle (**2**) has a global minimum of C_{2v} symmetry.

Geometry optimizations of the dicyano macrocycle (**3**) were also carried out. The macrocycle (**3**), with two cyano groups on its bridge carbon, was found to be a better model for macrocycle (**1**) than macrocycle (**2**), which has no cyano groups. More specifically, the geometric features of the macrocyclic moiety of the *trans*- and *cis*-isomers of macrocycle (**3**) and their lithium complex are similar to those of isomers of macrocycle (**1**) and their lithium complex.

There is little conformational change in the *cis*-isomer of macrocycle (**3**) upon complexation with a lithium cation. In contrast, the conformational structures between the *trans*-isomer and the lithium complex of macrocycle (**3**) are quite different from each other. Based on the energy profiles and vibrational frequencies, a conformational inversion in the lithium complexes seems to be plausible after lithium complexation. The difference in the vibrational frequencies corresponding to the movement of the lithium cation suggests that C_{2v}-like skeletons in the macrocyclic moiety have a stronger interaction between the lithium cation and the coordinating nitrogens than the C_{2h} structure.

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11 For the discussion in complexation ability of lithium cation to host molecules, it is straightforward to discuss binding energies. The binding energies of lithium cation and host molecules were compared between *trans*- and *cis*-isomers of macrocycles (**1**) and (**3**). It was found that there were no meaningful differences and it was not worthy to mention about the binding energies. Thus the conformational change was paid attention to for the discussion.

12 C_{2h} and C_{2v} structures for the lithium complexes of macrocycle (**2**) and related structures for macrocycle (**3**) (Figs. 4 and 5) are discussed. One of these structures has the lithium perching on one face of the macrocycle and will have a large dipole moment, while in the other the lithium is buried more or less in the plane. The relative energies of these structures may be strongly affected by solvation. Hori et al. discussed the solvent effect of water on the lithium ion selectivity of a crown ether, aza-12-crown-4 (*Tetrahedron*, **52**, 8199 (1996)). They reported that the stabilization energies for the complexes of aza-12-crown-4 with alkali metal cations (Li^+, Na^+) in water were different from those in gas phase. In this study, however, such solvent effect needs not to be taken into account because the solvent in this reaction is not water as a polar solvent but $CDCl_3$ having a small dielectric constant.

13 In order to examine the electronic correlation effect MP2 calculations were carried out at the RHF/3-21G structures. Estimated values of the energy barrier height for the conformational inversion of the macrocyclic moiety in macrocycle (**2**) and its lithium complex were, respectively, 15.58 and 5.17 kcal mol^{-1} (MP2/3-21G//RHF/3-21G). Thus the correlation energies for both the metal-free macrocycle and its lithium complex were estimated to be ca. 3 kcal mol^{-1}. The energy profiles based on the MP2 energies are similar to Fig. 6, though the MP2 energy barrier height was estimated to be higher than that of RHF.

14 This proposed process of lithium complexation does not mean that the lithium complexes are easier to make conformational inversion than the related metal-free macrocycles.

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