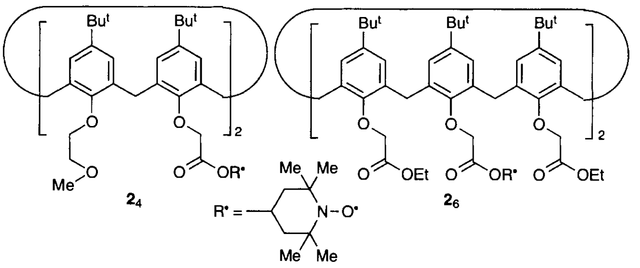
Metal-induced Conformational Changes in Calix[*n*]arenes can Change the Exchange Interaction between N–O· Radicals

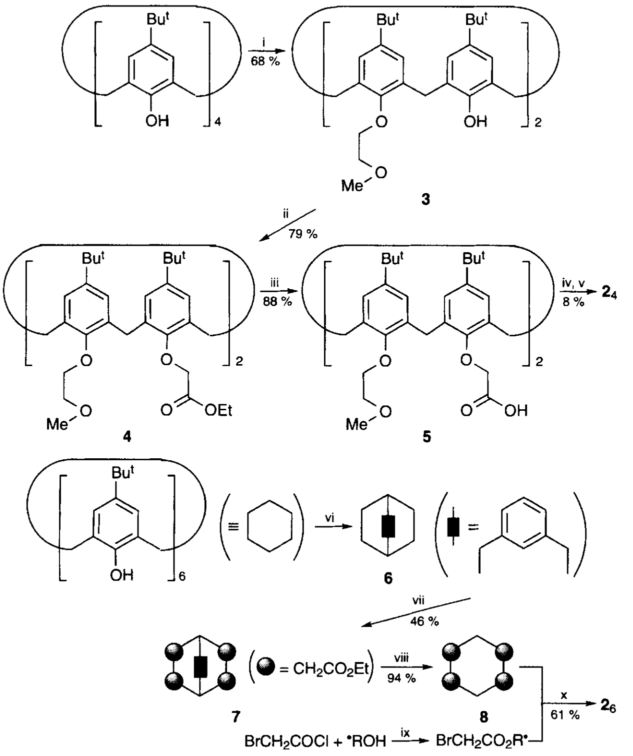
Koji Araki, Ryoji Nakamura, Hideyuki Otsuka and Seiji Shinkai*

Department of Chemical Science & Technology, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

Calix[*n*]aryl esters **2**$_n$ (*n* = 4 and 6) bearing two stable N–O·radicals on the lower rim are synthesized: in **2**$_6$ the exchange interaction (EI) changes in response to a metal-induced 1,2,3-alternate-to-cone conformational change but in **2**$_4$ the metal-induced rotation of the carbonyl groups is not enough to change the EI.

The exchange interaction (EI) among paramagnetic species plays crucial roles in designing ferromagnetic devices. We considered that if EI could show some response to stimuli from the outside world, it would lead to exploitation of intriguing magnet-functionalized materials with an on–off-type switch function. Several groups have devoted their research efforts towards this possibility.[1,2] We previously showed that conformational changes in calix[*n*]aryl esters **1**$_n$ can be readily induced by bound alkali metal cations.[3,4] In **1**$_4$, the carbonyl groups are directed outwards to reduce electrostatic repulsion among the C=O groups whereas the *exo*-annulus carbonyls are changed to the *endo*-annulus carbonyls to coordinate to bound Na$^+$. In **1**$_6$, the most stable conformation is 1,2,3-alternate but it is isomerized to the cone conformation in the presence of Cs$^+$ so that all carbonyl groups can coordinate to bound Cs$^+$.[5–7] These findings suggest that if stable radicals are introduced into the ester moieties as terminal groups (R), the radical–radical distance can be changed and EI can be controlled by added metal cations. To realize this idea we synthesized **2**$_4$ and **2**$_6$. Compound **2**$_4$ is conformationally immobilized as a cone and the change in distance occurs in response to the C=O rotation. Compound **2**$_6$ is still conformationally mobile but the two radical groups always adopt an *anti* position as long as it is kept in a 1,2,3-alternate conformation. On the other hand, when they adopt a *syn* position in the presence of alkali metal cations, the distance becomes shorter.





Scheme 1 *Reagents*: i, $BrCH_2CH_2OMe$, K_2CO_3, KI in DMF; ii, $BrCH_2CO_2Et$, NaH in THF and DMF; iii, Me_4NOH in H_2O and THF; iv, $(COCl)_2$ in CCl_4; v, 4-hydroxy-2,2,6,6-tetramethylpiperidino-1-oxy radical (·ROH), pyridine in THF; vi, α,α'-dibromo-*m*-xylene, NaH in THF and DMF; vii, $BrCH_2COOEt$, Cs_2CO_3 in acetone; viii, H_2, Pd–C in THF; ix, THF; x, Cs_2CO_3 in DMF

Compounds **2**$_4$ and **2**$_6$ were synthesized according to Scheme 1. The products were identified by IR spectral evidence and elemental analyses (the ^{1}H NMR spectra were broadened by the radical species and therefore useless). The radical purity was estimated using a calibration curve prepared from diphenylpicrylhydrazyl (DPPH) as a reference compound: 100% purity for **2**$_4$ and 84% purity for **2**$_6$.† Although the purity of **2**$_6$ was damaged by the last step reaction (Scheme 1), we considered that the impurity content is not so high as to affect

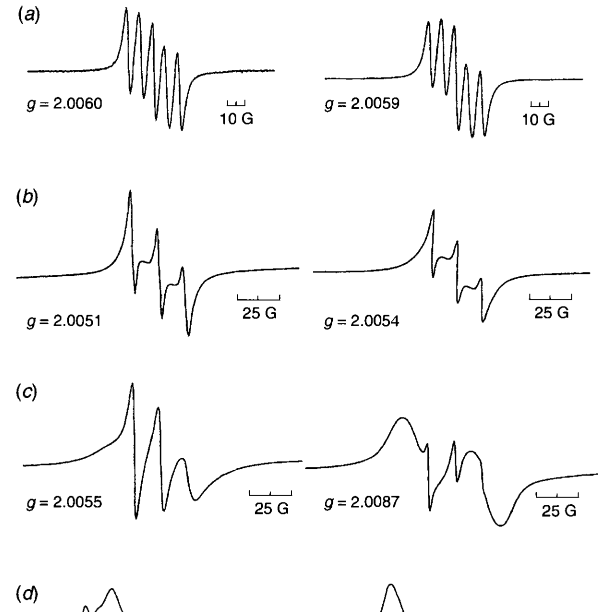


Fig. 1 EPR spectra of **2**$_4$ (1.00 mmol dm^{-3}) in the absence (left) and the presence (right) of $Ph_4B^-Na^+$ (4.00 mmol dm^{-3}) in THF–toluene (2 : 3 *v*/*v*). (*a*) 25; (*b*) −40; (*c*) −80; (*d*) −134 °C.

the EPR spectra and therefore it is still in the allowable range for the present purpose.

To confirm the conformation and the metal binding properties by an NMR spectroscopic method [$^2H_8$]THF, 400 MHz) we reduced the N–O·radicals to N–OH groups with phenylhydrazine.[8] In the presence of 4 equiv. of $Ph_4B^-Na^+$ the proton signals of reduced cone-$\mathbf{2}_4$ disappeared and the new proton signals assignable to the reduced cone-$\mathbf{2}_4 \cdot Na^+$ complex appeared. Reduced $\mathbf{2}_6$ gave one singlet and one pair of doublets in a 1 : 2 integral intensity ratio for the $ArCH_2Ar$ methylene protons. This indicates that $\mathbf{2}_6$ adopts a 1,2,3-alternate conformation. When 4 equiv. of $Ph_4B^-Cs^+$ were added, the splitting pattern for the $ArCH_2Ar$ protons was changed to two pairs of doublets in a 1 : 2 integral intensity ratio.‡ The result supports the view that the conformation is converted to cone through Cs^+ complexation.

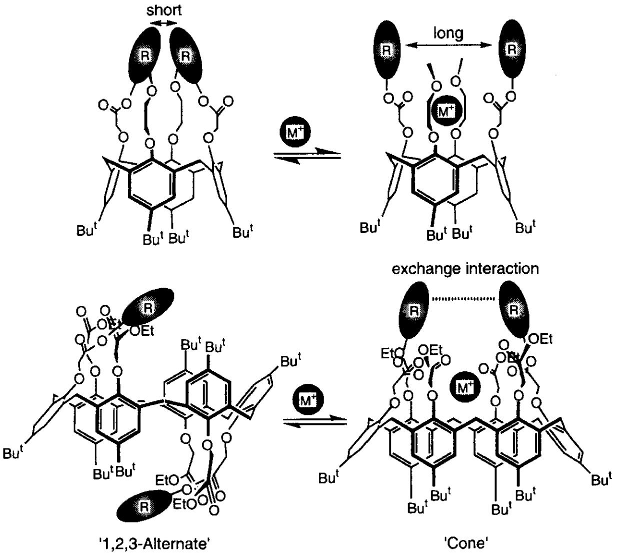


Fig. 2 Schematic representation of the metal-induced distance change between radical groups (R·) in $\mathbf{2}_4$ (*a*) and $\mathbf{2}_6$ (*b*). In 1,2,3-alternate-$\mathbf{2}_6$ the radical-carrying phenyl units do not necessarily occupy the central position in a 1,2,3 (or 4,5,6) array. However, even though they occupy the verge position in the array, they are still in an *anti* position.

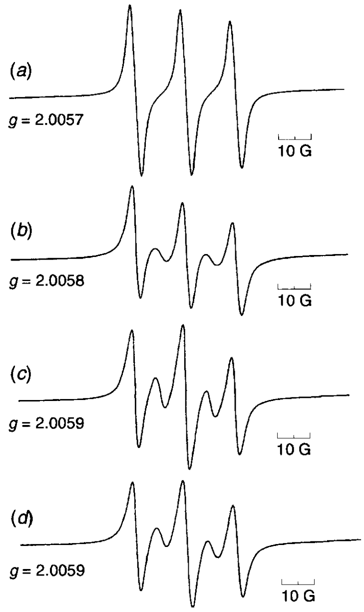


Fig. 3 EPR spectra of $\mathbf{2}_6$ (1.00 mmol dm^{-3}) in the absence and the presence of $Ph_4B^-M^+$ (4.00 mmol dm^{-3}) in THF at 25 °C. (*a*) No metal; (*b*) Cs^+; (*c*) Rb^+; (*d*) K^+.

The EPR measurements for $\mathbf{2}_4$ was carried out in THF–toluene (2 : 3 *v*/*v*): the mixed solvent was chosen to make the low-temperature measurement possible. As shown in Fig. 1, the EPR spectra gave a quintet resonance both in the absence and the presence of $Ph_4B^-Na^+$. The result indicates that EI does exist in $\mathbf{2}_4$ regardless of the absence or the presence of Na^+. Although the spectral shape is somewhat different (particularly at low-temperature region), the essential difference in EI cannot be induced by the Na^+-induced rotation of the carbonyl groups (Fig. 2). As demonstrated by monomer *vs.* excimer emission in a pyrene-functionalized calix[4]aryl ester,[3] the distance between two R· groups is shortened in the presence of Na^+. However, this distance change is obviously not sufficient to affect EI between two N–O·radicals.

We expected that the greater distance change would be realized in a metal-induced 1,2,3-alternate-to-cone conformational change in $\mathbf{2}_6$. Examination of CPK molecular models suggests that the distance between the two radicals in 1,2,3-alternate-$\mathbf{2}_6$ is further than that in the cone-$\mathbf{2}_4$ complex (*ca.* 2-fold). As shown in Fig. 3, $\mathbf{2}_6$ gave a triplet resonance indicating that the distance between two radical groups occupying the distal *anti*-position in the 1,2,3-alternate conformation is too far to enjoy EI. On the other hand, when the $\mathbf{2}_6$ conformation is converted to cone through metal cation complexation, cone-$\mathbf{2}_6$ gave an unsymmetrical quintet resonance. The result clearly indicates that the metal complexation can change the distance between two radical groups from the EI-free distance to the EI distance (Fig. 2). The clearest splitting (*i.e.* largest EI) was observed for Rb^+ and the next for K^+.‡

In conclusion, the present study established that EI between two radicals can be controlled by the metal-binding event occurring on a calixarene platform. We believe that this concept is applicable to the metal-control of various magnetic properties and eventually to the magnet-functionalized devices.

Received, 19th June 1995; Com. 5/03926F

Footnotes

† The results show that the last step to $\mathbf{2}_4$ (reaction of acid chloride and ·ROH) does not damage the radical species but the last step to $\mathbf{2}_6$ (reaction of phenolate anions with $BrCH_2COOR\cdot$) partially damages the radical species.

‡ We first expected that the $\mathbf{2}_6 \cdot K^+$ complex would result in the largest EI because the ester groups must be flattened to bind small K^+ ion. The results obtained herein show, however, that Rb^+ can induce larger EI than K^+. This implies that two bulky radical units in the $\mathbf{2}_6 \cdot K^+$ complex stand up and as a result, the radical distance is not necessarily shortest among alkali metal cations tested herein.

References

1 G. Gagnaire, A. Juenet and J.-L. Pierre, *Tetrahedron Lett.*, 1989, **30**, 6507; also see G. Gagnaire, A. Juenet and J.-L. Pierre, *Tetrahedron Lett.*, 1991, **32**, 2021.
2 H. Dugas, P. Keroack and M. Ptak, *Can. J. Chem.*, 1984, **62**, 489.
3 I. Aoki, T. Sakaki and S. Shinkai, *J. Chem. Soc., Chem. Commun.*, 1992, 730; T. Jin, K. Ichikawa and T. Koyama, *J. Chem. Soc., Chem. Commun.*, 1992, 499; also see A. Arduini, E. Ghidini, A. Pochini and R. Ungaro, *J. Inclusion Phenomen.*, 1988, **6**, 119.
4 H. Murakami and S. Shinkai, *J. Chem. Soc., Chem. Commun.*, 1993, 1533; H. Murakami and S. Shinkai, *Tetrahedron Lett.*, 1933, **34**, 4237.
5 S. Kanamathareddy and C. D. Gutsche, *J. Org. Chem.*, 1922, **57**, 3160.
6 H. Otsuka, K. Araki, T. Sakaki, K. Nakashima and S. Shinkai, *Tetrahedron Lett.*, 1993, **34**, 7275; A. Ikeda, T. Nagasaki and S. Shinkai, *J. Phys. Org. Chem.*, 1992, **5**, 699.
7 S.-Y. Han, M.-H. Kang, Y. E. Jung and S.-K. Chang, *J. Chem. Soc., Perkin Trans. 2*, 1994, 835.
8 T. D. Lee and J. F. W. Keana, *J. Org. Chem.*, 1975, **40**, 3145.
9 H. Otsuka, K. Araki and S. Shinkai, *Tetrahedron*, 1995, **51**, 8757.