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The influence of heteroatoms on the conformational properties of heteracalix[4]arenes. Comparison of oxygen-, sulfur-, and nitrogen-bridged [1_4]metacyclophanes

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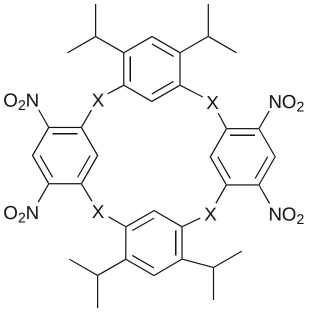
ABSTRACT

Oxygen- and sulfur-bridged calix[4]arenes have been synthesized by the nucleophilic aromatic substitution of 1,5-difluoro-2,4-dinitrobenzene with 4,6-diisopropylresorcinol or 4,6-diisopropyl-1,3-benzenedithiol. X-ray crystal structure analyses revealed that the oxacalix[4]arene **2** adopts an unsymmetrical 1,3-alternate conformation and that the dinitrobenzene rings strongly conjugate with the bridging oxygen atoms. On the other hand, the thiacalix[4]arene **3** adopts a heavily twisted unsymmetrical 1,3-alternate conformation, and the conjugation is very weak. In the ^{1}H NMR spectrum ($CDCl_3$, 30 °C), both compounds display a pair of diastereotopic methyl signals for the isopropyl groups in agreement with the frozen 1,3-alternate conformation on the NMR time scale. The free energies of activation ($\Delta G^{\#}_{298}$) of the macrocyclic inversion for **2** and **3** were determined to be 69.5 kJ mol^{-1} and 74.9 kJ mol^{-1}, respectively, by variable temperature NMR spectroscopy.

The calix[4]arenes are conformationally flexible macrocycles possessing a [1_4]metacyclophane scaffold.[1] The understanding of the preferred conformations and the dynamic conformational characteristics of the macrocycles is of importance in the design of various supramolecular systems. It is well understood that the conformational properties of calixarenes are dependent particularly upon the substituents at the intra-annular positions. These macrocycles can in principle adopt four basic conformations, namely *cone*, *partial cone, 1,3-alternate*, and *1,2-alternate,* that interconvert by rotation of a single phenyl unit by the 'lower-rim-through-annulus' mechanism. This interconversion is relatively easy when the lower rim is substituted by a small non-interacting group, for example, a methoxy group.[2] When the substituents become larger than an ethoxy group, the transition is sterically blocked and individual isomers can be isolated.[3]

Over the past few years, the synthesis of the heteroatom-bridged [1_n]metacyclophanes, that is, heteracalix[*n*]arenes, in which the methylene bridges between the aromatic units of calix[4]arenes are replaced by heteroatoms such as sulfur, oxygen, and nitrogen, has been studied with the aim of developing novel molecular scaffolds.[4] Such a replacement is expected to substantially change the conformational properties as a result of modification of the ring sizes and bond angles of the bridging atoms. Although the solid state structures of many of these heteracalix[4]arenes have been determined, the study of their dynamic conformational properties in solution is limited to a few systems.[5] Indeed, the conformational analysis of heteroatom-bridged calix[4]arene derivatives is not a trivial task due to the absence of CH_2 bridges, the signals of which are used in classical calix[4]arene stereochemistry. Thus, we have been interested in the conformational properties of the heteracalix[4]arene possessing four isopropyl groups at the extra-annular positions **1**–**3** (Fig. 1). Since the maximal attainable symmetry of these compounds is C_{2v} (cone, 1,3-alternate) or C_{2h} (chair)[6] in all conformations, no mirror symmetry plane can bisect the two geminal methyls within a given



1: X = NH
2: X = O
3: X = S

Figure 1. Heteracalix[4]arenes bearing diastereotopic geminal methyl groups for VT NMR spectroscopy.

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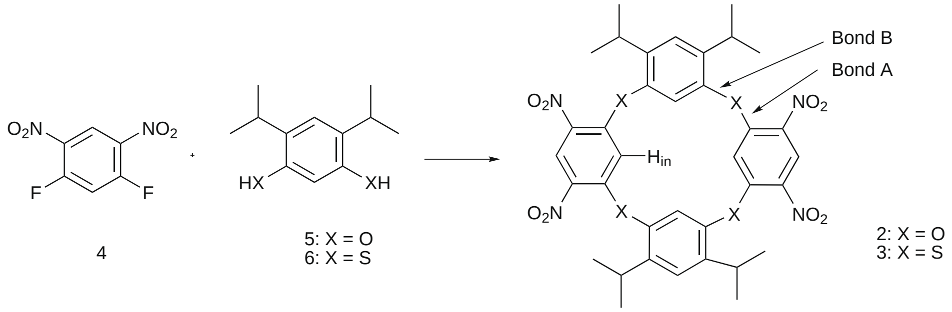


Scheme 1. Synthesis of heteracalix[4]arenes by aromatic nucleophilic substitution. Conditions for **2**:**4** (0.4 mmol), **5** (0.4 mmol), CsF (1.0 mmol), DMF (2.5 ml), 100 °C, 2 h; for **3**:**4** (1.1 mmol), **6** (1.1 mmol), K_2CO_3 (2.2 mmol), DMF (5 ml), 130 °C, 2 h.

isopropyl group. Therefore, the two methyl protons within each isopropyl group are diastereotopic, and possess different chemical shifts. On the other hand, when the molecular framework is mobile on the NMR time scale, rapid interconversion between the various conformers gives a time-averaged planar structure with a D_{2h} symmetry. Consequently, pairs of methyl protons within a given isopropyl group are enantiotropic, and possess the same chemical shift. Thus the determination of the rate of the macrocyclic ring inversion was made possible by monitoring of the spectral changes of the isopropyl methyl signals during variable temperature NMR spectroscopy.

In this Letter,[5d] we reported the conformational properties of the tetraisopropyltetranitroazacalix[4]arene **1**. In the solid state, it was found that the dinitrobenzene rings strongly conjugate with the bridging nitrogen atoms. Indeed, the freezing of the macrocyclic ring inversion was observed at room temperature during 400 MHz ^{1}H NMR spectroscopy. Our present contribution continues the program aimed at understanding the effect of the conjugation of the dinitrobenzene rings with the bridging heteroatoms and the steric effects of the substituents at the intra- and/or extra-annular positions on the conformational properties of [1_4]metacyclophane. We now report the synthesis, structural features, and VT ^{1}H NMR spectra of oxacalix[4]arene **2** and thiacalix[4]arene **3**.

The heteracalix[4]arenes were synthesized by aromatic nucleophilic substitution (Scheme 1).[7] The oxacalix[4]arene **2** was synthesized by aromatic nucleophilic substitution of an equimolar amount of 1,5-difluoro-2,4-dinitrobenzene with 4,6-diisopropylresorcinol in the presence of CsF (2 mol equiv) in DMF at 100 °C for 2 h.[8] Analogously, the thiacalix[4]arene **3** was synthesized by the reaction of 1,5-difluoro-2,4-dinitrobenzene with 4,6-diisopropyl-1,3-benzenedithiol in the presence of K_2CO_3 in DMF at 130 °C for 2 h.[9] The structures of **2** and **3** were conclusively identified by an X-ray analysis.[10] Crystals of **2** and **3** suitable for the X-ray diffraction analysis were obtained by recrystallization from toluene (for **2**) or DMSO (for **3**). Their ORTEP drawings are shown in Figure 2.

The structural parameters relevant to the conformational features of these heteracalix[4]arenes are summarized in Table 1. One of the most remarkable structural aspects of the macrocycles is the deviation of the four bridging heteroatoms from their mean plane. In the solid state of **1**, the four nitrogen atoms at the bridging positions are nearly located in the mean plane defined by these atoms with a maximum deviation of 0.045 Å. Moreover, four oxygen atoms of **2** are on the same plane with a deviation from planarity of 0.001 Å. In contrast, in **3**, the sulfur atoms are not arranged on their mean plane but deviate up and down by about 0.86 Å. In all cases, the diisopropylbenzene rings are nearly parallel; the dihedral angles between the opposite rings for **1**, **2**, and **3** are 18.8°, 15.0°, and 1.7°, respectively. Meanwhile, the dinitrobenzene rings are oriented outward, and the dihedral angles between the two opposite rings for **1**, **2**, and **3** are 114.2°, 123.9°, and 67.9°, respectively. Briefly, **1** and **2** adopt an unsymmetrical 1,3-alternate conformation, whereas **3** adopts a heavily twisted unsymmetrical 1,3-alternate conformation.

In these compounds, the bonds A between the bridging heteroatom and dinitrobenzene ring are shorter than the bonds B between the bridging heteroatom and diisopropylbenzene (see Scheme 1). The differences in these bond lengths for **1**, **2**, and **3** are 0.087, 0.051, and 0.021 Å, respectively. The significant shortening of bond A observed in **1** and **2** indicate that the bridging heteroatoms strongly conjugate with the dinitrobenzene rings. A similar tendency of the bridging heteroatoms to form conjugation with electron-deficient aromatic rings has been reported in the heteracalix[*n*]arene[*n*]hetarene system.[11] Besides, in these compounds, the C–X–C angles and the torsion angles of bond A also demonstrate a significant sp^2 hybrid character at the N and O atoms. In contrast, in compound **3**, although bond A is slightly shortened, the C–X–C angles (102.5°) and the torsion angles of bond A (24.2°) imply that the conjugation of the dinitrobenzene rings with the sulfur atoms is very weak. Furthermore, the comparison of the average C–S bond lengths of **3** and the parent thiacalix[4]arene **7** (Fig. 3)[12], both 1.77 Å, indicates that the introduction of four nitro groups does not influence the C–S bond length.

The ^{1}H NMR spectrum of oxacalix[4]arene **2** ($CDCl_3$, 500 MHz at 30 °C) showed a couple of methyl doublets (1.09 and 1.21 ppm) and one methine septet (2.93 ppm) for the isopropyl groups, and four singlets for the aromatic protons. In addition, its ^{13}C NMR spectra ($CDCl_3$, 125 MHz at 30 °C) showed two methyl signals at 22.3 and 23.3 ppm. These data revealed that the inversion of the macrocycle is restricted on the NMR time scale. The intra-annular protons (H_{in}, see Scheme 1) resonate at 5.88 ppm, indicating that the H_{in} protons were significantly affected by the ring current of the neighboring diisopropylbenzene rings. Thus, the preferred conformation of **2** is presumed to be similar to that observed in the crystal structure. Similar characteristic spectral features have been observed for **1**, where the H_{in} protons appear at 5.30 ppm.

The thiacalix[4]arene **3** showed two methyl signals in the ^{1}H NMR spectrum ($CDCl_3$, 400 MHz at 30 °C); 1.12 and 1.26 ppm, and in the ^{13}C NMR spectrum ($CDCl_3$, 125 MHz at 30 °C); 22.0 and 25.6 ppm. These spectral features also demonstrated the rigidity of the macrocyclic framework of **3**. Unexpectedly, the large upfield shifts of H_{in} found in **1** and **2** could not be observed in **3**, in which the H_{in} protons appeared at 6.85 ppm. A similar chemical shift for the H_{in} protons (6.71 ppm) in the tetranitrothiacalix[4]arene **8** in DMSO-d_6 at 80 °C was reported.[13] The similarity of the chemical shifts of these protons suggests that the preferred conformations of **3** and **8** are similar and that the isopropyl groups have little effect on the conformation in solution. These much smaller high field chemical shifts are probably due to the smaller dihedral angle between the opposite dinitrobenzene rings of **3**

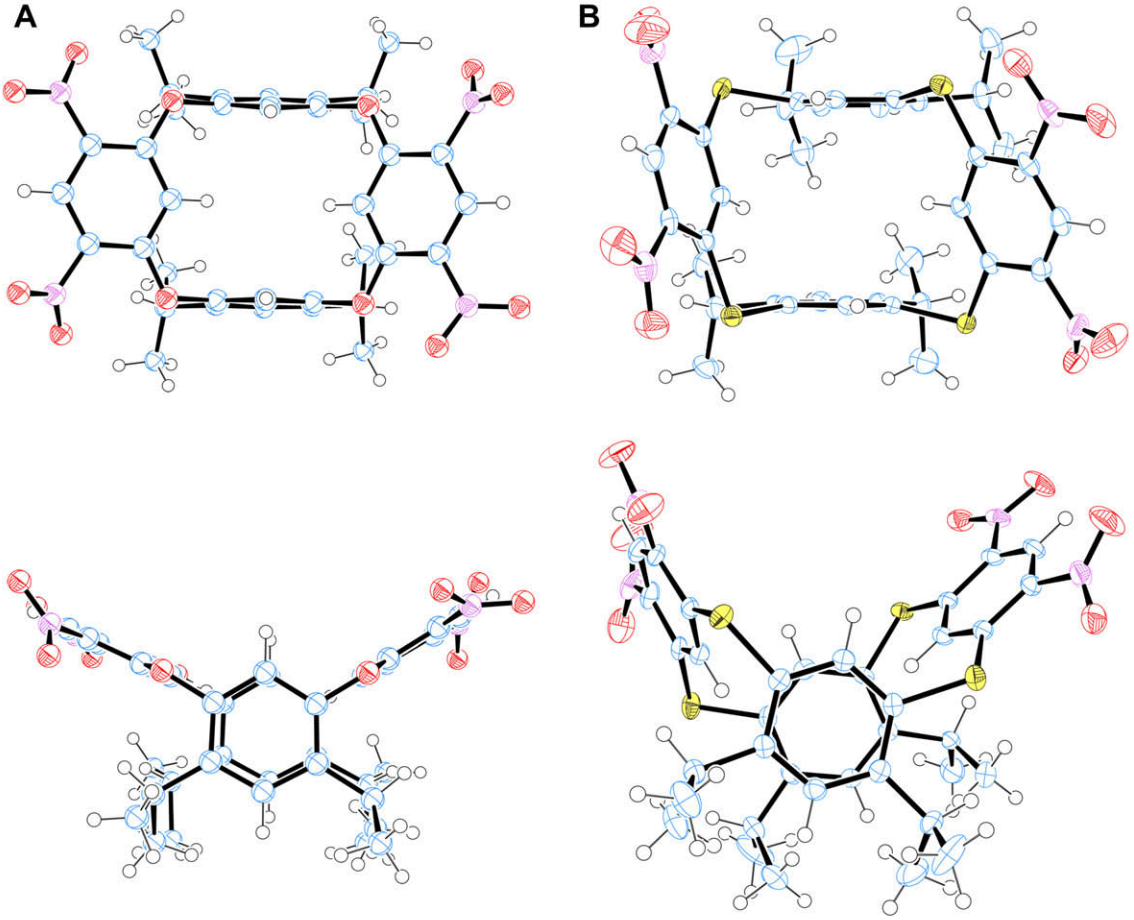


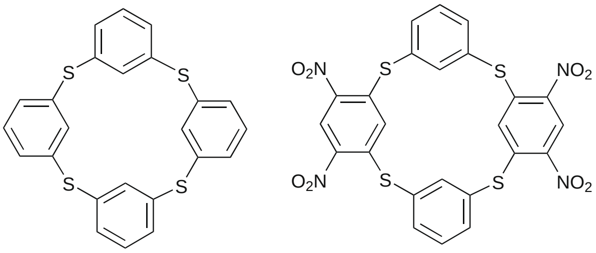
Figure 2. X-ray crystal structure of (A) **2** and (B) **3** with thermal ellipsoids drawn at the 50% probability level. Atom coloring: O, red; N, magenta; S, yellow; C, blue; and H, white. Solvent molecules are omitted for clarity.

Table 1
Structural features of heteracalix[4]arenes **1**–**3**

	1	2	3
Deviation of heteroatoms from the mean plane (Å)			
	0.044	0.001	0.858
	−0.045	−0.001	−0.861
	0.044	0.001	0.869
	−0.044	−0.001	−0.866
Dihedral angles between opposite dinitrobenzene rings (°)			
	111.4	123.9	67.9
Dihedral angles between opposite diisopropylbenzene rings (°)			
	18.8	15.0	1.7
Average bond lengths (Å)			
bond A	1.351	1.359	1.762
bond B	1.438	1.410	1.783
Average C–X–C angle (°)			
	123.5	118.2	102.5
Average torsion angle around bond A (°)			
	5.3	7.0	24.2

compared with **1** or **2**. In such a conformation, it is presumed that the H_{in} protons do not locate in the shielding region of the neighboring aromatic rings.

The dynamic conformational properties of **2** and **3** were observed by variable temperature ^1H NMR spectroscopy. The VT ^1H NMR spectra of the isopropyl methyl signals of **2** and **3** in DMSO-d_6 in the temperature range from 323 K to 423 K are shown in Figure 4 (left) and Figure 5 (left), respectively. These methyl signals gradually became broad as the temperature increased,



7

8

Figure 3. Thiacalix[4]arenes.

whereas the methine signals did not change. These findings are indicative of a 1,3-alternate to 1,3-alternate inversion of the macrocycles. The line-shape simulations[14] of the isopropyl methyl signals as an A_3M_3X spin system along with the ring inversion rate constants (k) for **2** and **3** are shown in Figure 4 (right) and Figure 5 (right), respectively. The Eyring plots, ln (k/T) versus 1000/T, are shown in Figure 6 and the thermodynamic parameters, activation enthalpy $\Delta H^{\neq}$, activation entropy $\Delta S^{\neq}$, and activation free energy $\Delta G^{\#}_{298}$, and the rate constants at 298 K are listed out in Table 2 and compared to the azacalixarene **1**. The flexibility of the macrocycles based on the $\Delta G^{\#}_{298}$ is in the order of **1** (87.5 kJ mol^{-1}) < **3** (74.9 kJ mol^{-1}) < **2** (69.5 kJ mol^{-1}). These values are much higher than that of the methylene-bridged calix[4]arenes. For example, the $\Delta G^{\neq}$ value for the calix[4]arene bearing no substituents at

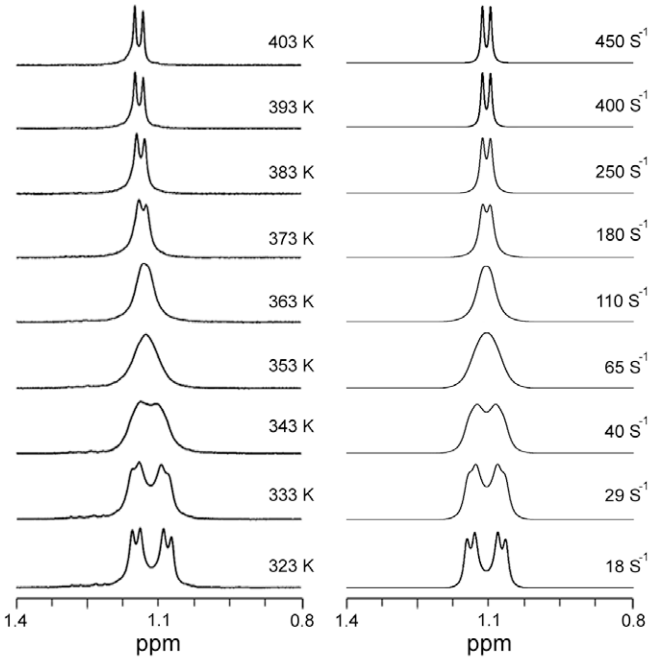


Figure 4. Left: temperature-dependent ^{1}H NMR spectra of the isopropyl methyl signals of **2** at 400 MHz in DMSO-d_6. Right: line-shape simulations obtained using the indicated rate constants.

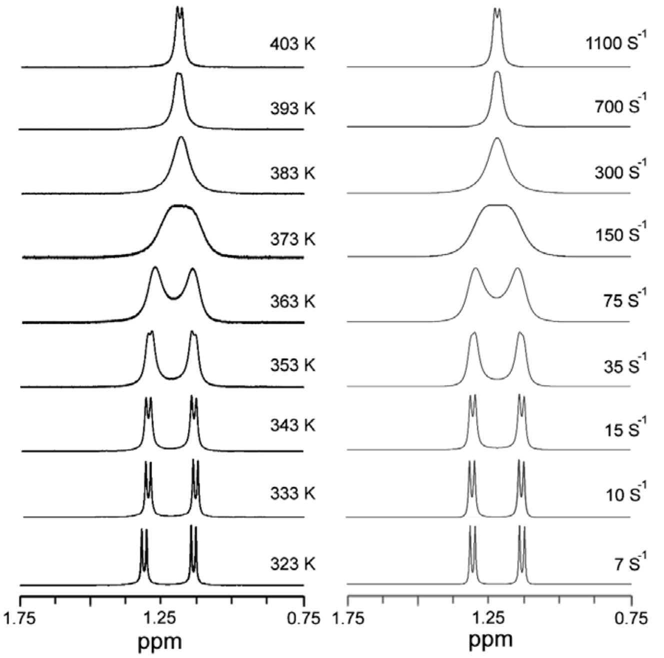


Figure 5. Left: temperature-dependent ^{1}H NMR spectra of the isopropyl methyl signals of **3** at 400 MHz in DMSO-d_6. Right: line-shape simulations obtained using the indicated rate constants.

the intra-annular position 9 (X = H) is less than 24.7 kJ mol^{-1}.[15] The sequence of the flexibility is quite different from the order of the increasing average bond lengths of the bridging atoms to aromatic carbons, that is, **2** (C–O, 1.39 Å) < **1** (C–N, 1.40 Å) < **9** (C–C, 1.54 Å) < **3** (C–S, 1.77 Å).

One of the factors for controlling the flexibility of **1**, **2**, and **3** is the conjugation of the dinitrobenzene rings with the bridging heteroatoms. In the case of **1**, this conjugation significantly stabilizes

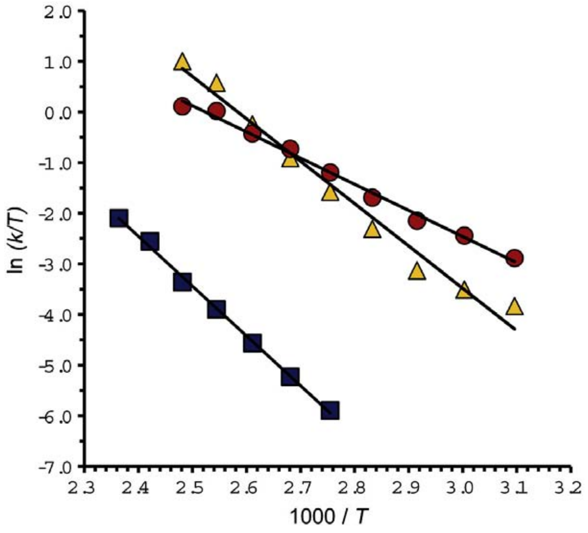
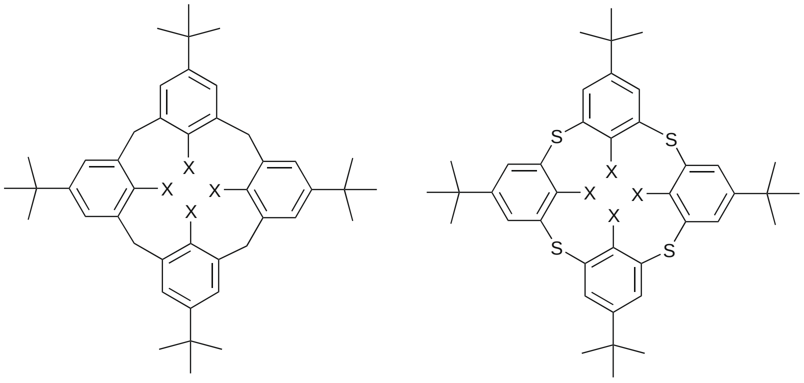


Figure 6. Eyring plots for the ring inversion of 1(■), 2 (●), and 3 (▲) obtained from VT ^{1}H NMR experiments in DMSO-d_6 at 400 MHz.

Table 2
Thermodynamic parameters and rate constants for the ring inversion of **1**, **2**, and **3** in DMSO-d_6

Compound	$\Delta H^{\neq}$/ kJ mol^{-1}	$\Delta S^{\neq}$/J K^{-1} mol^{-1}	$\Delta G^{\neq}$ (298 K)/ kJ mol^{-1}	k (298 K)/ s^{-1}
1	78.0	−31.8	87.5	2.4×10^{-3}
2	43.0	−89.0	69.5	4.0
3	69.6	−17.7	74.9	4.6×10^{-1}

the ground state conformation, resulting in the high inversion barrier. Since the molecular structure of **2** is similar to that of **1**, the higher flexibility of **2** may be ascribed to the somewhat weak conjugation of the dinitrobenzene rings with the bridging oxygen atoms. Most interestingly, the ring inversion of **2** (k = 4.0 s^{-1}) is faster than that of **3** ($k = 4.6 \times 10^{-1}$ s^{-1}) at 298 K. In the case of the phenol-derived calix[4]arenes (Fig. 7), the thiacalix[4]arenes **10** (X = OH, OMe, OEt) are more flexible than the corresponding methylene-bridged compounds **9**.[16] The higher mobility of **10** has been accounted for by their longer C–S bond length in comparison with the C–C bond length. Since the average C–S bond length of **3** is equal to that of **10** and there is no remarkable conjugation of the dinitrobenzene rings with the bridging sulfur atoms, we anticipated that the thiacalix[4]arene **3** is much more flexible than **1** and **2**. This unexpected result indicates that the major factor for reducing the flexibility of **3** is the steric hindrance between the nitro group and the isopropyl group on the adjacent aromatic rings during the transition state for the ring conversion. Indeed, the large activation free energy is mainly due to the unfavorable enthalpy effect of the transition state for the ring inversion ($\Delta H^{\neq}$ 69.6 kJ mol^{-1}). Similar situations are observed in mesitylene-derived calixarenes.[17] In addition, it is of interest to note the temperature dependence of the inversion rates of **2** and **3**. As shown in Figures 4 and 5, the ring inversion of **3** is faster than that of **2** above 383 K. The high barrier for **2** seems to be reflected in the more negative entropy ($T\Delta S^{\neq}$) contributions to the activation energy ($\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq}$). Since the negative $\Delta S^{\neq}$ value is indicative of a crowded transition state, it is presumed that the transition state for **2** is more severely crowded than that for **3** due to the smaller annuli. The van der Waals radius of the bridging heteroatoms X, bond lengths C–X, and bond angles C–X–C are the important structural factors that influence the dynamic conformational properties.



9 **10**

Figure 7. Calix[4]arenes bearing *tert*-butyl substituents at their extra-annular positions.

In summary, we have demonstrated the comparison of the conformational properties of the heteroatom-bridged tetraisopropyltetranitrocalix[4]arenes **1**, **2**, and **3** in solution and in the solid state. Variable temperature NMR spectroscopy and X-ray crystallography revealed that the conjugation between the dinitrobenzene rings and the bridging heteroatoms and/or the steric repulsion between the substituents at the extra-annular positions play an important role in increasing the inversion barrier of the macrocycles. These results emphasize the complex interplay between the substituents and the heteroatoms that must be taken into account in the conformational analysis of the heteracalix[4]arene chemistry.

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6. The *anti*-isomer of tetranitrooxacalix[4]arene bearing two propyl groups at its intra-annular distal positions adopts a chair conformation, where the two opposite dinitrobenzene rings are almost coplanar with the least square plane defined by the four bridging oxygen atoms (see Ref. 7c).
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8. $1^4,1^6,5^4,5^6$-Tetraisopropyl-$3^4,3^6,7^4,7^6$-tetranitro-2,4,6,8-tetraoxa-1,3,5,7-tetrabenzenacyclooctaphane (**2**): A mixture of 4,6-diisopropylresorcinol (0.4 mmol, 86 mg), 1,5-difluoro-2,4-dinitrobenzene (0.4 mmol, 90 mg), and CsF (1.0 mmol, 146 mg) in DMF (2.5 ml) was stirred at 100 °C for 2 h under Ar. After cooling, $CHCl_3$ and water were added. The organic layer was separated, washed with water, and then dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was dissolved in chloroform and then subjected to GPC separation to produce the pure oxacalix[4]arene **2** (63 mg, 40%). Mp 249 °C (dec). IR (KBr) 2966, 1616, 1589, 1533, 1489, 1354, 1288, 1192, 1053, 831 cm^{-1}. 500 MHz ^{1}H NMR ($CDCl_3$, 30 °C) δ 1.09 (d, 12H, J = 7.0 Hz, –CH(CH_3)$_2$), 1.21 (d, 12H, J = 7.0 Hz, –CH(CH_3)$_2$), 2.93 (sept, 4H, J = 7.0 Hz, –*CH*(CH_3)$_2$), 5.88 (s, 2H, H_{in}), 6.63 (s, 2H, ArH), 7.31 (s, 2H, ArH), 8.88 (s, 2H, ArH). 125 MHz ^{13}C NMR ($CDCl_3$, 30 °C) δ 22.3 (CH_3), 23.3 (CH_3), 27.6 (CH), 102.6, 114.5, 126.3, 126.9, 132.0, 140.3 148.4, 156.9.
9. $1^4,1^6,5^4,5^6$-Tetraisopropyl-$3^4,3^6,7^4,7^6$-tetranitro-2,4,6,8-tetrathia-1,3,5,7-tetrabenzenacyclooctaphane (**3**): A mixture of 4,6-diisopropylbenzenedithiol (1.1 mmol, 247 mg), 1,5-difluoro-2,4-dinitrobenzene (1.1 mmol, 225 mg), and K_2CO_3 (2.2 mmol, 311 mg) in DMF (5 ml) was stirred at 130 °C for 2 h under Ar. After cooling, ethyl acetate and water were added. The organic layer was separated, washed with water, and then dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was dissolved, and purified by GPC separation to produce the pure thiacalix[4]arene **3** (71 mg, 17%). Mp 256 °C (dec). IR (KBr) 2964, 2360, 2341, 1708, 1583, 1566, 1523, 1496, 1338, 1294, 831 cm^{-1}.400 MHz ^{1}H NMR ($CDCl_3$, 30 °C) δ 1.12 (d, 12H, J = 7.0 Hz, –CH(CH_3)$_2$), 1.26 (d, 12H, J = 7.0 Hz, –CH(CH_3)$_2$), 3.16 (sept, 4H, J = 7.0 Hz, –*CH*(CH_3)$_2$), 6.85 (s, 2H, H_{in}), 7.33 (s, 2H, ArH), 7.44 (s, 2H, ArH), 9.18 (s, 2H, ArH). 125 MHz ^{13}C NMR ($CDCl_3$, 30 °C) δ 22.0 (CH_3), 25.6 (CH_3), 31.2 (CH), 124.2, 125.4, 126.2, 127.2, 141.2, 142.4 144.9, 155.5.
10. *X-ray crystal structure analysis*: The X-ray data were collected at 173 K using a Rigaku R-AXIS RAPID-S imaging plate area detector with graphite monochromated Mo$K\alpha$ (λ = 0.7107 Å) radiation using the ω scan mode. The structure was solved by direct methods with SIR-92[18] (for **2**) and SHELX-97[19] (for **3**). Non-hydrogen atoms were anisotropically refined. All calculations were performed using the Crystal structure 3.8.2 crystallographic software package.[20] Crystallographic data in cif format (Refs. CCDC 727903 for **2**, 727904 for **3**) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystals of **2** were obtained by recrystallization from toluene: $C_{36}H_{36}O_{12}N_4 \cdot C_7H_8$, M = 808.84, orthorhombic, space group $Pna2_1$ (No. 33), a = 11.596(2), b = 18.790(3), c = 18.830(3), V = 4103.0(12) Å^3, Z = 4, ρ_c = 1.309 g cm^{-3}, 2θ$_{max}$ = 54.8°. F(0 0 0) = 1704. A total of 35,469 reflections were measured, 9333 were unique. The final cycle of full-matrix least squares refinement was based on all observed reflections, 533 variable parameters, with factors of R = 0.0678, wR_2 = 0.1480, GOF = 1.022, max/min. residual electron density 0.36/−0.28 Å^3. Crystals of **3** were obtained by recrystallization from dimethylsulfoxide: $C_{36}H_{36}O_8N_4S_4$, M = 780.94, monoclinic, space group $P2_1/n$ (No. 14), a = 11.682(1), b = 21.051(1), c = 15.762 (1), β = 104.849(3), V = 3746.7(4) Å^3, Z = 4, ρ_c = 1.384 g cm^{-3}, 2θ$_{max}$ = 55°. F(0 0 0) = 1632. A total of 35,348 reflections were measured, 8565 were unique. The final cycle of full-matrix least squares refinement was based on all observed reflections, 470 variable parameters, with factors of R = 0.0780, wR_2 = 0.1466, GOF = 0.981, max/min. residual electron density 0.54/−0.46 Å^3.
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