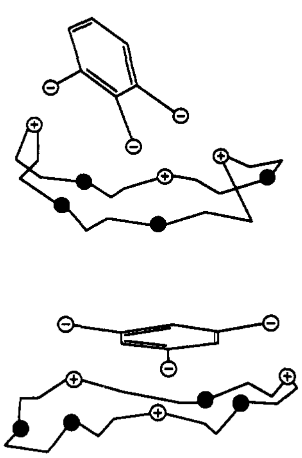
Scheme II



also display relatively rigid structures because of their simple conformational equilibria. Both **3** and **4** and their mono- and dianions adopt the chair conformations with the three or two *cis*-carboxyl groups axial. For the trianions, the conformer with the three or two *cis*-carboxylate groups equatorial is found to be the most stable[11] (Scheme I).

The basicity constants for the tricarboxylates and the stability constants for the complexes formed have been determined in aqueous solution by potentiometry at 298.15 K in 0.15 mol dm^{-3} NaClO$_4$.[12] The stepwise stability constants relative to the interaction of [21]aneN$_7$ with the tricarboxylate anions (A), as well as the basicity constants, are presented in Table I.

The first aspect to be noticed is that substrates **1**–**4** interact with [21]aneN$_7$ much stronger than the more flexible citrate anions used as a reference. A straight comparison between citrate and 1,2,3-benzenetricarboxylate anions can be made since their basicities are comparable. All of the stepwise stability constants for substrate **2** are about 3 orders of magnitude greater than those for citric acid (**5**). This figure represents one of the highest selectivities reported up to now ($K(\mathbf{2})/K(\mathbf{5}) > 1000$) in the interaction of polycarboxylate anions with polyammonium receptors in aqueous solution.[1,2,6] A direct comparison between **1**, **3**, **4**, and **5** could be difficult because of the different basicities involved, but distribution diagrams calculated from the constants revealed a situation very similar to that found in the former case, the percentage of bound substrate being much higher for **1**–**4** than for **5** at any pH value.

When comparing both aromatic acids (**1** and **2**), some points can be highlighted. The equivalence of the stepwise stability constants for the complexes H$_3$LA in both acids is remarkable. These species represent the interaction of the tricarboxylate with the triprotonated macrocycle. If electrostatic factors were the only ones controlling the interaction, the stability constants associated with the tricarboxylate of **2** would always be much higher than those for the trianion of **1**. In order to explain this situation, molecular modeling studies have been undertaken. Preliminary results[13] suggest a very good structural complementarity of the tricarboxylate of **1** and triprotonated [21]aneN$_7$. But in the case of the trianion of **2**, an appropriate interaction would require a partial unfavorable folding of the receptor. Thus, it seems that the better structural factor of **1** compensates the higher charge density of **2**. For more protonated complexes, a moderate selectivity of **2** over **1** is always observed (Scheme II).

Finally, the case of the two isomers **3** and **4** can be considered. Some selectivity is observed even for the interaction of the tricarboxylates with the triprotonated ligand ($K(\mathbf{3})/K(\mathbf{4}) = 8$). In the cis,cis isomer, the three carboxyls on the same side of the cyclohexane ring are better disposed for hydrogen bonding. Selectivity is maintained throughout the pH range, and distribution diagrams show how, for the same conditions, the percentages of complexed species are much greater in the case of the cis,cis isomer.

Further work is in progress to study in more detail the structural aspects of those interactions. However, the present results clearly show how preorganization of the substrate in a shape that could be complementary to that of the receptor can be of major importance in host–guest chemistry, giving rise to very high selectivities even in aqueous solution, and how minor structural changes, when producing complementarity differences, do affect selectivity so as to permit the selective recognition of one epimer over the other.

Acknowledgment. We are indebted to IVEI and DGICYT (PB90-0567) for financial support.

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(10) Compounds **3** and **4** were prepared as described by Rebek: Rebek, J., Jr.; Marshall, L.; Wolak, R.; Parris, K.; Killoran, M.; Askew, B.; Nemeth, D.; Islam, N. *J. Am. Chem. Soc.* **1985**, *107*, 7476–7481. Rebek, J., Jr.; Askew, B.; Killoran, M.; Nemeth, D.; Lin, F.-T. *J. Am. Chem. Soc.* **1987**, *109*, 2426–2431. Askew, B.; Ballester, P.; Buhr, C.; Jeong, K. S.; Jones, S.; Parris, K.; Williams, K.; Rebek, J., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 1082–1090. For leading references to molecular receptors based on Kemp's triacid see: Rebek, J., Jr. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 245–255.

(11) The Δδ for the nonequivalent methylene hydrogens permits monitoring of the conformational equilibria. For **3**, differences of 1.50 (triacid), 1.41 (monosodium salt), 1.31 (disodium salt), and 0.60 ppm (trisodium salt) are obtained (ref 9). For **4** and its mono- and dianion, differences of ca. 1.4 ppm are found for the two hydrogens of the methylene group situated between the two equivalent carboxyls, and a difference of only 0.46 ppm is found for the trianion.

(12) Potentiometric measurements were carried out in aqueous solutions at 298.15 K in 0.15 mol dm^{-3} by using equipment already described (see ref 8). The program SUPERQUAD was used to calculate the stability constants: Gans, P.; Sabatini, A.; Vacca, A. *J. Chem. Soc., Dalton Trans.* **1985**, 1195–1200. The titration curves for each system were treated as a single set or separately without significant variations in the values of the constants.

(13) MMX as implemented in PCMODEL, Serena Software, Bloomington, IN.

Corannulene Bowl-to-Bowl Inversion Is Rapid at Room Temperature

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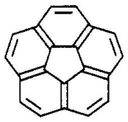
Our recent development of a convenient new route to corannulene (**1**)[1] and derivatives thereof (see below) has enabled us to measure the bowl-to-bowl inversion barrier for this archetypical curved network of trigonal carbon atoms.



1
Corannulene

The 300-MHz ^{1}H NMR spectrum of racemic corannulenyldimethylcarbinol (**2**)[2] in acetone-d_6 shows a single sharp peak for the diastereotopic methyl groups at room temperature (δ 1.87) but two well-resolved singlets at −90 °C (Δν = 39.2 Hz). The coalescence temperature for these two signals was found to be −64 °C (209 K), from which we calculate the barrier for bowl-to-bowl inversion in **2** to be $\Delta G^{\ddagger} = 10.2 \pm 0.2$ kcal/mol at this temperature.[3] Unless this barrier has a significant negative $\Delta S^{\ddagger}$ com-

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[†] Visiting scholar from Sharif University of Technology, Tehran, Iran.

(1) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082–7083.

(2) Corannulenyldimethylcarbinol (**2**) was prepared in routine fashion from bromocorannulene (**4**) by sequential treatment with *n*-BuLi and acetone, all at −78 °C in THF (40% yield based on unrecovered starting material). The product (**2**) was purified by preparative TLC on silica gel (10% EtOAc–hexane): ^{1}H NMR (300 MHz, acetone-d_6) δ 8.60 (d, 1 H, J = 9.0 Hz, H-10), 8.07 (s, 1 H, H-2), 7.96–7.91 (m, 7 H, H-3,4,5,6,7,8,9), 1.87 (s, 6 H, CH$_3$), 1.21 (s, 1 H, OH); high-resolution mass spectrum calcd for C$_{23}$H$_{16}$O 308.1201, found 308.1209.

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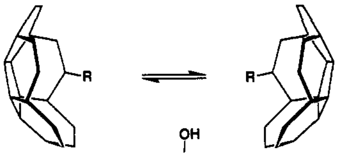
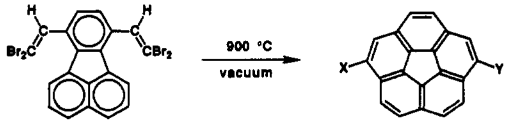
ponent, the corannulene ring system must invert more than 200 000 times per second at room temperature!


2 $R = \overset{OH}{C}(CH_3)_2$

$\Delta G^{\ddagger}$ (-64 °C) = 10.2 kcal/mol

The inversion barrier for **2** stands remarkably close in energy to that for inversion of cyclohexane from one chair conformation to another ($\Delta G^{\ddagger} = 10.3$ kcal/mol at −67 °C);[4] it lies lower in energy than the barrier for inversion of cyclooctatetraene from one tub conformation to another ($\Delta G^{\ddagger} = 14.7$ kcal/mol at −2 °C),[5] but exceeds the barrier for pyramidal inversion of ammonia ($\Delta G^{\ddagger} = 6.0$ kcal/mol)[6] by a significant amount. Corannulene shares with ammonia the structural requirement that each nonplanar trigonal atom must pass through a planar configuration (pure sp^2 hybridization) during the inversion process; however, the planarizations need not necessarily all occur contemporaneously during the bowl-to-bowl inversion of corannulene.[7] Calculations on the difference in energy between the bowl and the planar conformations of corannulene have ranged over the years from 0.8[8a] to 70.9 kcal/mol.[8b] The most recent ab initio calculations, however, peg it at 8.8 (STO-3G and 6-31G*),[9] 10.3 (3-21G),[9] and 11.0 kcal/mol (LDF).[10]

Painless access to substituted corannulenes was made possible by our fortuitous discovery that 7,10-bis(2,2-dibromovinyl)fluoranthene (**3**), which gives corannulene (**1**) upon flash vacuum pyrolysis at 1000 °C/10^{-4} Torr,[1] also gives bromocorannulene (**4**) and 1,6-dibromocorannulene (**5**) when the pyrolysis is conducted under only modest vacuum (mechanical pump) with a slow bleed of N_2 admitted through the head of the sample chamber as a carrier gas.[11] At this early stage in the project, the yields of **1**, **4**, and **5** still vary unpredictably from one pyrolysis to the next, but in one run at 900 °C, 50 mg of **3** gave 5.1 mg of **1** (23%), 10.3 mg of **4** (29%), and 1.2 mg of **5** (2.4%). These three compounds were separated and purified by preparative TLC (silica gel/cyclohexane) and characterized by 300-MHz ^1H NMR and high-resolution mass spectroscopy.[12]

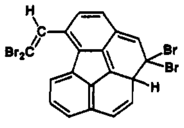


3

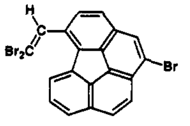
1: X = Y = H
4: X = H, Y = Br
5: X = Y = Br

We suspect that 1,6-dibromocorannulene (**5**) constitutes the primary product in this reaction and that **1** and **4** represent secondary products formed by pyrolytic loss of bromine atoms from **5**. Consistent with this hypothesis is our observation that other brominated aromatics, e.g., 1-bromonaphthalene, do indeed suffer reductive debromination to a major extent under the pyrolysis conditions employed here, although the origin of the hydrogen atom that replaces the bromine remains obscure.

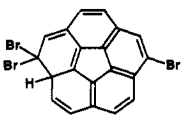
The initial formation of **5** can reasonably be explained by electrocyclic ring closure of **3** to give the pentacyclic intermediate **6**, which should spontaneously aromatize to **7** by loss of HBr. Repetition of these steps on the other side of the molecule would lead via **8** to 1,6-dibromocorannulene (**5**). An alternative mechanism involving cyclization reactions of vinyl radicals, generated by homolysis of C–Br bonds, can also be envisaged; however, no direct evidence is presently available on the mechanisms of these transformations.



6



7



8

We are continuing to explore the potentially fascinating chemistry of corannulene and its derivatives, especially the π-complexing ability of these substances, both with metals and with organic partners, e.g., C_{60} and other corannulenes inter alia.

Acknowledgment. We thank the Department of Energy for financial support of this work and Lewis Cary for conducting the low-temperature NMR measurements. The open exchange of data, advice, and manuscripts with Jay Siegel has been especially valuable and enjoyable. Helpful discussions with Dieter Wege and John H. Nelson are also gratefully acknowledged.

Registry No. 1, 5821-51-2; **2**, 138816-08-7; **3**, 135584-70-2; **4**, 138816-09-8; **5**, 138816-10-1.

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(3) Repetition of the NMR experiment in a 1:1 mixture of acetone-d_6–CD_2Cl_2 gave the same value for $\Delta G^{\ddagger}$. The ±0.2 kcal/mol error range we attach to this number reflects our conservative estimates of the possible errors in determining the true coalescence temperature and the maximum peak separation at the low-temperature limit. This variable-temperature NMR experiment is closely patterned after the classic work of Anet et al.,[5] who likewise measured the coalescence temperature of NMR signals from diastereotopic methyl groups on a dimethylcarbinol side chain to determine the barrier for tub-to-tub inversion in the cyclooctatetraene ring system.

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(5) Anet, F. A. L.; Bourn, A. J. R.; Lin, Y. S. *J. Am. Chem. Soc.* **1964**, *86*, 3576–3577.

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(7) Wynberg, H.; Nieuwpoort, W. C.; Jonkman, H. T. *Tetrahedron Lett.* **1973**, 4623–4628.

(8) (a) Kao, J. *J. Am. Chem. Soc.* **1987**, *109*, 3817–3829. See also the earlier work of Kao, J.; Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 975–986. (b) Gleicher, G. J. *Tetrahedron* **1967**, *23*, 4257–4263.

(9) Schulman, J. M.; Peck, R. C.; Disch, R. L. *J. Am. Chem. Soc.* **1989**, *111*, 5675–5680. Schulman, J. M. Private communication.

(10) Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.*, following paper in this issue.

(11) Flash vacuum pyrolyses were conducted in a commercially available Trahanovsky pyrolysis apparatus purchased from Kontes, Inc., Vineland, NJ 08360. The sample head was modified to allow a slow bleed of nitrogen gas to pass over the sample from a capillary inlet.

(12) Bromocorannulene (**4**): ^1H NMR (300 MHz, $CDCl_3$) δ 8.03 (s, 1 H, H-2), 7.93 (d, 1 H, *J* = 8.6 Hz, H-10), 7.87 (d, 1 H, *J* = 8.6 Hz, H-9), 7.82–7.78 (m, 5 H, H-4,5,6,7,8), 7.71 (d, 1 H, *J* = 8.6 Hz, H-3); high-resolution mass spectrum calcd for $C_{20}H_9Br$ 327.9887, found 327.9873. 1,6-Dibromocorannulene (**5**): ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (s, 2 H, H-2,5), 7.97 (d, 2 H, *J* = 8.7 Hz, H-7,10), 7.90 (d, 2 H, *J* = 8.7 Hz, H-8,9), 7.72 (s, 2 H, H-3,4); high-resolution mass spectrum calcd for $C_{20}H_8Br_2$ 405.8992, found 405.8982.

Synthesis and Dynamics of the Corannulene Nucleus

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Corannulene (**1**), first synthesized by Lawton and Barth,[2] has presented a formidable synthetic challenge to several groups in-

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(1) (a) University of California at San Diego. (b) San Diego Supercomputer Center.

(2) (a) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 380. (b) Barth, W. E.; Lawton, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1730.

0002-7863/92/1514-1921$03.00/0