Theoretical Studies of the Inversion Barrier in Corannulenes

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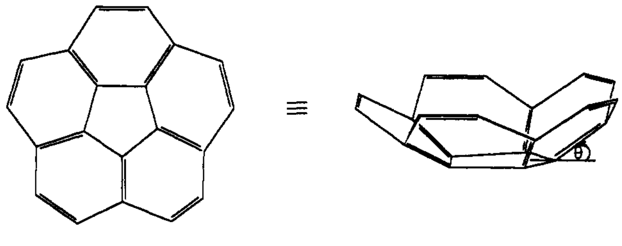
Abstract: Ab initio energies and geometries of symmetrical corannulenes having carbons selectively substituted by heteroatoms are reported. It is found that substitution can greatly affect the inversion barrier: pentaazocorannulene has a barrier 8 times that of corannulene, while in pentaborazacorannulene it is less than 1 kcal/mol. A very small barrier is also found for the tetraanion of corannulene. For corannulene itself, vibrational frequencies are reported for its equilibrium bowl (C_{5v}) and planar (D_{5h}) forms at the 6-31G* SCF level. All 84 vibrational frequencies of the bowl form are real. Planar corannulene has one imaginary (A_2'') frequency, strongly suggesting that it is the transition state for bowl-to-bowl inversion. The energies, vibrational frequencies, and moments of inertia provide estimates of the enthalpy and free energy of activation for inversion. $T\Delta S^{\ddagger}$ is positive and ca. 12% of $\Delta H^{\circ}_{\mathrm{f},298}$ at 298 K. $\Delta H^{\circ}_{\mathrm{f},298}$ of corannulene is calculated to be 122.1 kcal/mol.

Corannulene (**1**), first synthesized in the pioneering work of Barth and Lawton,[1] is an aromatic hydrocarbon revealed by X-ray diffraction to be a bowl-shaped molecule with C_{5v} symmetry.[2] Ab initio SCF calculations, which produced a C_{5v} structure in good agreement with the X-ray geometry, predicted a barrier for bowl-to-bowl inversion through the D_{5h} form of 9–10 kcal/mol.[3] Experimental confirmation of the relatively low barrier has been made possible by new synthetic routes to corannulenes recently reported by Scott et al.[4] and Borchardt et al.[5] Using ^{1}H NMR measurements, Scott et al.[4] obtained $\Delta G^{\ddagger} = 10.2 \pm 0.2$ kcal/mol for the inversion of the dimethylcarbinol derivative of corannulene in acetone solution at 209 K. Borchardt et al.[5] synthesized corannulene and its dihydro and tetrahydro derivatives. The latter two are bowl-shaped molecules with $\Delta G^{\ddagger} = 8.5$ and 6–7 kcal/mol, respectively. These authors calculated inversion barriers for corannulene and its hydrogenated derivatives by the local density–functional method, obtaining good agreement with experiment. Most recently, Rabideau and co-workers[6] have obtained an inversion barrier not less than 26 kcal/mol in a corannulene having two adjacent benzene rings tethered by an ethano bridge.



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The resurgence of interest in corannulenes leads us to report further theoretical results on inversion barriers in corannulene-like molecules. It is shown that selective substitution of carbons with heteroatoms may strongly affect the barrier height, increasing it greatly or reducing it nearly to zero.

In the second part of this paper, we report the ab initio vibrational frequencies of **1** in both its bowl and planar forms at the 6-31G* SCF level.[7] These frequencies confirm that the C_{5v} and D_{5h} forms of corannulene are a minimum and a transition state, respectively, on the $C_{20}H_{10}$ potential surface. Together with the moments of inertia of the two structures, they allow a calculation of $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$ for the inversion process as a function of temperature.

Methods

The bowl-shaped and planar geometries of the molecules studied here were optimized in the STO-3G, 3-21G, and 6-31G* basis sets using programs developed by us for IBM System/370 machines. The bowl forms are of C_{5v} or C_5 symmetry and their planar counterparts are D_{5h} or C_{5h}. The vibrational frequencies of C_{5v} and D_{5h} corannulene were computed at the 6-31G* SCF level. After scaling, as described below, thermodynamic functions were calculated from the frequencies and moments of inertia. The heat of formation of corannulene is calculated using group equivalents derived for benzenoid hydrocarbons.[8]

Heterocorannulenes

Replacement of selected carbons by heteroatoms offers a means of modulating inversion effects in corannulenes. The heterocorannulenes studied include **2**, **3**, and **4**, which are isoelectronic with **1**, and the pentaazacorannulenium ion (**5**), a monocation isoelectronic with the recently reported tetraanion of corannulene (**6**).[9] The calculated total energies for the bowl and planar forms are given in Table 1, together with the inversion barriers, $\Delta H^{\ddagger}$, under the assumption that these species invert along pathways of C_{5v} or C_5 symmetry.

Pentaiminocorannulene (**2**) and pentaazocorannulene (**3**) have $\Delta H^{\ddagger} = 43.3$ and 99.3 kcal/mol, respectively, at the 6-31G* SCF level. Both inversion barriers are substantially greater than the ca. 10 kcal/mol barrier found for **1**. At the other extreme is pentaborazacorannulene (**4**), whose barrier to inversion is less than 1 kcal/mol; the potential energy surface in the vicinity of its minimum is quite flat, making the location of the global

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[1] (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.

[2] Hanson, J. C.; Nordman, C. E. *Acta Crystallogr.* **1976,** *B32,* 1147.

[3] (a) Schulman, J. M.; Peck, R. C.; Disch, R. L. *J. Am. Chem. Soc.* **1989,** *111,* 5675. (b) Peck, R. C.; Schulman, J. M.; Disch, R. L. *J. Phys. Chem.* **1990,** *94,* 6637.

[4] (a) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991,** *113,* 7082. (b) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc.* **1992,** *114,* 1920.

[5] Borchardt, A.; Fuchicello, A.; Kilway, K. V.; Baldridge, K. K.; Siegel, J. S. *J. Am. Chem. Soc.* **1992,** *114,* 1921.

[6] Abdourazak, A. H.; Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1993,** *115,* 3010.

[7] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley and Sons: New York, 1986.

[8] Disch, R. L.; Schulman, J. M.; Peck, R. C. *J. Phys. Chem.* **1992,** *96,* 3998.

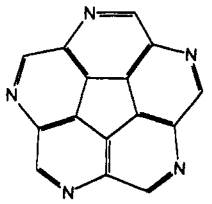
[9] Ayalon, A.; Rabinovitz, M.; Cheng, P.-C.; Scott, L. T. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 1636.

0002-7863/94/1516-1533$04.50/0

Table 1. Ab Initio Energies and Inversion Barriers

molecule	symmetry	θ (deg)	basis	energy (–au)	$\Delta H^{\ddagger\,a}$ (kcal/mol)
1	C_{5v}	21.0	6-31G*	763.1893	
		22.6	3-21G	758.9082	
			3-21G(RMP2)	760.6405	
		20.7	STO-3G	753.9035	
	D_{5h}	0.0	6-31G*	763.1752	8.8
			3-21G	758.8915	10.5
			3-21G(RMP2)	760.6152	15.9
			STO-3G	753.8893	8.9
2	C_5	31.1	6-31G*	843.1057	
		30.3	3-21G	838.3399	
			3-21G(RMP2)	840.1743	
		28.9	STO-3G	832.5985	
	C_{5h}	0.0	6-31G*	843.0357	43.9
			3-21G	838.2841	35.0
			3-21G(RMP2)	840.1129	38.5
			STO-3G	832.5456	33.2
3	C_{5v}	37.9	6-31G*	922.7778	
		36.1	3-21G	917.4711	
			3-21G(RMP2)[c]	919.4625	
		34.5	STO-3G	911.1427	
	D_{5h}	0.0	6-31G*	922.6196	99.3
			3-21G	917.3567	71.8
			3-21G(RMP2)[c]	919.3705	57.7
			STO-3G	911.0434	62.3
4	C_5	9.9	6-31G*	780.4412	
		8.0	3-21G	776.1374	
			3-21G(RMP2)	777.7786	
		13.0	STO-3G	770.8385	
	C_{5h}	0.0	6-31G*	780.4406	0.4
			3-21G	776.1375	–0.1[d]
			3-21G(RMP2)	777.7774	0.8
			STO-3G	770.8368	1.1
5[b]	C_{5v}	19.2	6-31G*	845.6138	
		19.9	STO-3G	835.2140	
	D_{5h}	0.0	6-31G*	845.6018	7.5
			STO-3G	835.1975	10.4
6[b]	C_{5v}	8.8	3-21G	757.8753	
		4.6	STO-3G	752.3358	
	D_{5h}	0.0	3-21G	757.8748	0.3
			STO-3G	752.3358	0.0

[a] The barrier is the energy of the planar transition state relative to the bowl form. [b] The charges on molecular ions **5** and **6** are +1 and –4, respectively. [c] Calculated at the 3-21G SCF geometry. [d] The flat potential surface favors the planar structure at the 3-21G SCF level.



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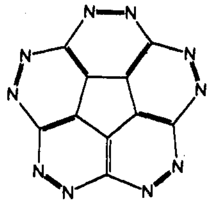

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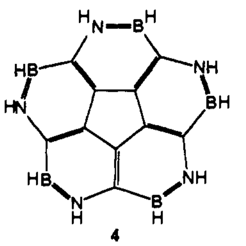

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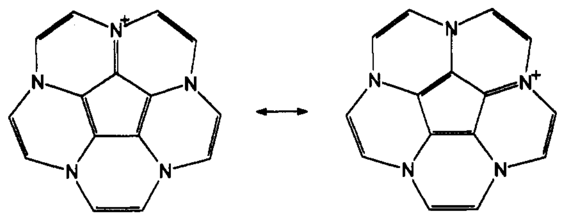
minimum uncertain. Pentaazacorannulenium ion (**5**), two of whose resonance structures are indicated, has $\Delta H^{\ddagger}$ = 7.5 kcal/mol, which is essentially the value found for **1**, despite the presence of four additional π electrons.



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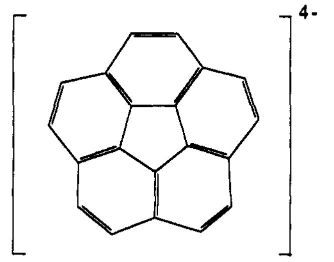

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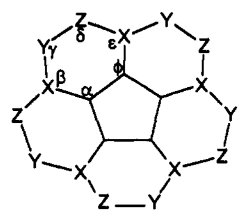
The SCF barrier heights of **2** and **3** are sensitive to the basis set. In **3**, the STO-3G $\Delta H^{\ddagger}$, 62.3 kcal/mol, is ca. 37 kcal/mol smaller than the 6-31G* value. Geometry optimization at the 3-21G SCF level furnishes an intermediate value, 71.8 kcal/mol.

The barrier heights were also calculated at the frozen-core RMP2/3-21G(RMP2)//3-21G level. While this or any non-polarized basis has known deficiencies for the description of electron correlation, these computations can indicate trends in the barriers. At the RMP2 level, the inversion barrier of corannulene increases to 15.9 kcal/mol, while that for **2** remains essentially the same. In contrast, the barrier for **3** is lowered by 14 kcal/mol due to inclusion of electron correlation. In 6-31G*(RMP2), the reduction could be 20 kcal/mol or more, given that the virtual space consists of 235 MOs vs 115 in 3-21G. Even a reduction of more than 20 kcal/mol leads to a barrier in excess of 70 kcal/mol.[10] It is, of course, possible that **3** can invert by a less symmetric pathway having a smaller $\Delta H^{\ddagger}$.

Geometric parameters of the heterocorannulenes are given in Table 2. 6-31G* values of the bowl elevation angle, θ, for **2**, **3**, **4**, and **5** are 31.1°, 37.9°, 9.9°, and 19.2°, respectively. The value for corannulene is 21.0°, similar to the X-ray value of 22.4°.[2] The height of the inversion barrier is correlated with the extent of deviation from planarity ($\theta = 0$), consistent with larger changes in bond angles and bond lengths upon flattening for molecules with larger θ values. Bonds XY, XZ, and YZ (Figure 1) lengthen in going to the transition state, while CC and CX decrease. For the bond angles, α and ϕ increase, β and ϵ decrease. In the case of pentazocorannulene (**3**), CC, CN, and NN bond lengths change by 0.055, 0.053, and 0.064 Å, respectively; $\alpha = \phi$ and $\beta = \epsilon$ change by 8.4 and –9.3°, respectively. Given the large number of these bonds, it is not difficult to see why the inversion barrier in **3** is high, especially when compared to **1**, in which the framework bond lengths change by less than 0.02 Å.



1 X=C, Y=CH, Z=CH
2 X=C, Y=N, Z=CH
3 X=C, Y=N, Z=N
4 X=C, Y=NH, Z=BH
5 X=N, Y=CH, Z=CH, 1+
6 X=C, Y=CH, Z=CH, 4-

Figure 1. Labeling scheme for corannulene and the heterocorannulenes.

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(10) The AM1 method gives an inversion barrier of 89 kcal/mol of 3.

Table 2. 6-31G* SCF Geometric Parameters of the Corannulenes

parameter[a]	1	2	3	4	5
			Bond Lengths (Å)		
CC	1.412 (1.395)	1.416 (1.377)	1.414 (1.359)	1.425 (1.422)	1.368 (1.353)
CX	1.360 (1.346)	1.354 (1.320)	1.346 (1.293)	1.343 (1.343)	1.380 (1.362)
XY	1.450 (1.463)	1.458 (1.500)	1.389 (1.453)	1.397 (1.399)	1.366 (1.372)
XZ	1.450 (1.463)	1.378 (1.406)	1.389 (1.453)	1.567 (1.570)	1.366 (1.372)
YZ	1.370 (1.382)	1.300 (1.317)	1.260 (1.284)	1.435 (1.439)	1.389 (1.409)
			Bond Angles (deg)		
α	122.0 (126.0)	120.2 (126.8)	117.6 (126.0)	125.6 (125.7)	123.7 (126.0)
β	114.1 (111.0)	114.4 (107.4)	120.0 (110.7)	113.6 (113.2)	112.3 (109.7)
γ	122.0 (123.0)	124.0 (125.9)	120.3 (123.3)	125.6 (125.9)	123.6 (124.3)
δ	122.0 (123.0)	118.9 (121.4)	120.3 (123.3)	117.4 (117.6)	123.6 (124.3)
ϵ	114.1 (111.0)	114.4 (107.4)	120.0 (110.7)	112.3 (111.3)	112.3 (109.7)
ϕ	122.0 (126.0)	120.2 (125.2)	117.6 (126.0)	125.2 (126.3)	123.7 (126.0)
θ[b]	21.0 (0.0)	31.1 (0.0)	37.9 (0.0)	9.9 (0.0)	19.2 (0.0)
			Dihedral Angles (deg)		
XCCC	154.6 (180.0)	143.2 (180.0)	136.1 (180.0)	167.8 (180.0)	156.7 (180.0)
CCXY	9.2 (0.0)	12.8 (0.0)	16.5 (0.0)	–4.9 (0.0)	7.1 (0.0)
CCXZ	–9.2 (0.0)	–13.6 (0.0)	–16.5 (0.0)	4.4 (0.0)	–7.1 (0.0)
XYZX	0.0 (0.0)	1.2 (0.0)	0.0 (0.0)	–0.5 (0.0)	0.0 (0.0)
CXYZ	–9.0 (0.0)	–13.9 (0.0)	–16.9 (0.0)	4.9 (0.0)	–7.0 (0.0)
CXZY	9.0 (0.0)	12.8 (0.0)	16.9 (0.0)	–4.1 (0.0)	7.0 (0.0)
XCCX	0.0 (0.0)	0.0 (0.0)	0.1 (0.0)	0.1 (0.0)	0.0 (0.0)

[a] The parameters are defined in Figure 1. Values for the planar structures are in parentheses. [b] The angle between the CX bond and its projection onto the basal pentagonal plane.

Table 3. Scaled 6-31G* Harmonic Frequencies of Corannulene (cm^{-1})[a]

D_{5h}		C_{5v}	
A_1'	527, 1011, 1218, 1445, 1711, 3072	A_1	143, 545, 587, 873, 1024, 1277, 1440, 1656, 3058
A_2''	90,[b] 608, 950		
A_2'	642, 929, 1208, 1471, 3050	A_2	542, 634, 923, 999, 1215, 1496, 3050
A_1''	553, 992		
E_1'	377, 727, 843, 1148, 1170, 1298, 1421, 1442, 1709, 3051, 3070	E_1	316, 397, 457, 672, 738, 839, 853, 1003, 1151, 1183, 1305, 1419, 1457, 1665, 3043, 3062
E_1''	299, 453, 675, 846, 995		
E_2'	419, 542, 591, 1037, 1099, 1135, 1354, 1402, 1506, 1730, 3052, 3069	E_2	164, 289, 422, 533, 597, 638, 795, 814, 1013, 1044, 1120, 1149, 1353, 1400, 1484, 1681, 3034, 3065
E_2''	165, 308, 611, 791, 822, 1002		

[a] Each species of the D_{5h} structure is placed opposite its correlated species of the C_{5v} structure. [b] Imaginary frequency.

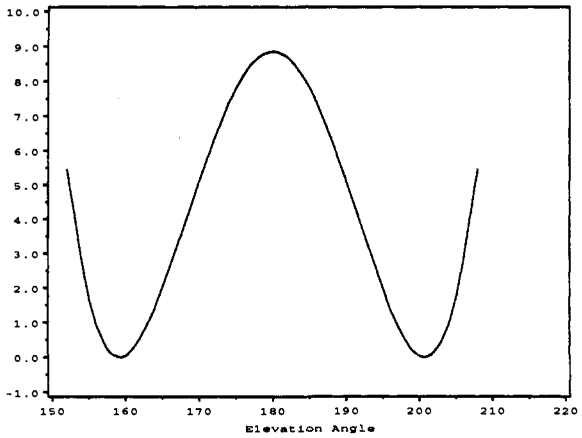

Figure 2. Energy as a function of the elevation angle, θ, for the interconversion of C_{5v} corannulene via a D_{5h} transition state.

Calculation of ΔG^* for the Inversion of Corannulene

From Table 1, the 6-31G* energies of C_{5v} and D_{5h} corannulene are respectively –763.1893 and –763.1752 au, the energy difference being 8.8 kcal/mol. Using group equivalents for benzenoid aromatics[8] and the 6-31G* total energies of **1**, ΔH_f° is 122.1 kcal/mol for the bowl form and 130.9 for the planar structure.

The 6-31G* vibrational frequencies of C_{5v} and D_{5h} corannulene were obtained at their optimized geometries. Frequencies at this level tend to exceed the experimental values by ca. 10%. In this study, they were scaled by 0.91, bringing the calculated zero-point energies into agreement with the value given by an empirical formula relating the ZPE of a hydrocarbon to its stoichiometry, 142.6 kcal/mol.[11] The scaled 6-31G* ab initio frequencies of C_{5v} and D_{5h} corannulene are given in Table 3. There are 84 real frequencies for the C_{5v} form, the lowest being 143 and 164 cm^{-1} for A_1 and E_2 modes, respectively. The D_{5h} form has a single imaginary frequency for a mode of A_2'' symmetry, which connects the two C_{5v} forms. In view of the good estimate of the barrier for inversion provided by ab initio theory, it is safe to say that the D_{5h} structure is the transition state for inversion. Figure 2 depicts the energy of corannulene as a function of the elevation angle θ along a pathway of C_{5v} symmetry.

From the partition functions in the ideal gas and rigid rotor approximations,[12] the thermal corrections to the enthalpies of C_{5v} and D_{5h} corannulene are found to be 7.8 and 7.5 kcal/mol, respectively, at 298 K. The ZPEs of the C_{5v} and D_{5h} forms of corannulene are 142.6 and 142.3 kcal/mol, respectively, the ZPE correction to ΔH^* being –0.3 kcal/mol. Thus, ΔH^* is 8.8 – 0.6 = 8.2 kcal/mol. The vibrational entropies of the C_{5v} and D_{5h} structures are 28.0 and 25.5 eu, respectively, so $\Delta S^*_{\mathrm{vib}} = -2.5$ eu at 298 K. Calculation of the rotational entropies requires use of the moments of inertia of C_{5v} and D_{5h}, symmetric rotors with symmetry numbers 5 and 10. For C_{5v} corannulene at its 6-31G* geometry, with y as the 5-fold axis, $I_{xx} = I_{zz} = {}^1/_2 I_{yy} = 1669.2790 \times 10^{-40}\ \mathrm{gm \cdot cm^2}$; the corresponding value for D_{5h} corannulene is 1636.2208. $\Delta S^*_{\mathrm{rot}}$ is calculated to be –1.5 eu; therefore, $\Delta S^* = -4.0$ eu.

At 298 K, in kcal/mol, $-T\Delta S^* = 1.2$, $\Delta H^* = 8.2$, and $\Delta G^* = 9.4$. The latter is larger than the ab initio energy difference, 8.8, by 0.6 kcal/mol. Thus, calculated ab initio values of $\Delta H^‡$ for

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(11) Schulman, J. M.; Disch, R. L. *Chem. Phys. Lett.* **1985**, *113*, 291.

(12) Davidson, N. *Statistical Mechanics*; McGraw-Hill: New York, 1962.

corannulenes should be less than those of $\Delta G^{\ddagger}$ by no more than 1 kcal/mol. While an exact comparison with experiment is not possible at this time, it is of interest that $\Delta G^{\ddagger}$ calculated at 209 K (9.1 kcal/mol) is in better agreement than $\Delta H^{\ddagger}$ with the experimental value for the dimethylcarbinol derivative of corannulene in acetone solution at 209 K, $\Delta G^{\ddagger} = 10.2 \pm 0.2$ kcal/mol.[4]

Discussion

This study shows that it is possible to have a large range of bowl-to-bowl inversion barriers in heterocorannulenes and that $\Delta H^{\ddagger}$ gives a good estimate of $\Delta G^{\ddagger}$ for molecules possessing a corannulene-like framework. Although we have chosen corannulenes with heteroatoms in multiples of 5 in order to retain 5-fold symmetry, it is reasonable to suppose that even when fewer heteroatoms are present, $\Delta H^{\ddagger}$ could differ significantly from that of **1**.

Wiberg and co-workers[13] have found that 6-31G* CN bond lengths vary from 1.310 to 1.320 Å in six monocyclic azines, including pyridazine. The CN bond length in planar **3**, 1.453 Å, is 0.13 Å larger. The angles $\alpha = \phi$, which are 126° in the planar structures, would lead to large increases in the NN bond lengths of **3**, were it not for elongation of the CN and contraction of the CC bonds. Similarly, β and ϵ decrease from their nominal value, 120°. The strain in these bond lengths and bond angles is smaller in their bowl structures, and this is most probably the source of the high $\Delta H^{\ddagger}$ of **3** (and **2**). A somewhat different situation occurs in planar pentaborazacorannulene (**4**). The BN bond (1.439 Å) is unstretched relative to its value in borazine, 1.44 Å.[14] The CB bond length, 1.570 Å, is large compared to that of borepin,[15] 1.537 Å; while the CN bond length of 1.399 Å is farther from the azine CN range of 1.310–1.320, it is not as far as in **2** and **3**. Thus, the lower inversion barrier in **4** may be ascribed to the smaller strain relief in passing to the bowl form.

A few remarks are in order on the tetraanion **6**, which has been prepared as its tetralithium salt in THF solution. As reported in Table 2, we find a slightly nonplanar structure, $\theta = 4.6°$, in STO-3G, but it is one whose energy is only 0.03 kcal/mol below that of the planar form. In the 3-21G basis, $\theta = 8.8°$ and the barrier increases slightly to 0.3 kcal/mol. Because the study of anions usually requires that diffuse atomic orbitals be included in the basis, we calculated the energy of both the C_{5v} and the D_{5h} forms of the tetraanion in the 6-311G basis[7] at the 3-21G geometries. While the use of the 6-31+G basis is preferred, convergence in this basis is impeded by very small eigenvalues, ranging over more than 8 orders of magnitude, of the overlap matrix. The 6-311G total energies of the two structures, –762.0622 and –762.0612 au, differ by only 0.6 kcal/mol. The root mean square Cartesian gradients, 0.0007 and 0.0006 au/bohr indicate that geometry optimization in the 6-311G basis would have little effect upon this result. Thus, at the SCF level, the tetraanion is predicted to be slightly distorted from planarity, but to an extent which would be difficult to confirm experimentally. The planarity is not, however, a consequence of either the number of π electrons (**5**, which is isoelectronic with **6**, has a barrier of 8–10 kcal/mol, nearer to that of **1** than to **6**) or the large charge (model calculations on the pentaprotonated form of **2** give $\Delta H^{\ddagger} = 8.9$ kcal/mol in STO-3G).

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(13) Wiberg, K. B.; Nakaji, D.; Breneman, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 4178.

(14) Leroy, G.; Sana, M.; Wilante, C. *Theor. Chim. Acta* **1993**, *85*, 155.

(15) Schulman, J. M.; Disch, R. L. *Organometallics* **1989**, *8*, 733.