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Conformational Studies in the Cyclohexane Series. 2. Phenylcyclohexane and 1-Methyl-1-phenylcyclohexane

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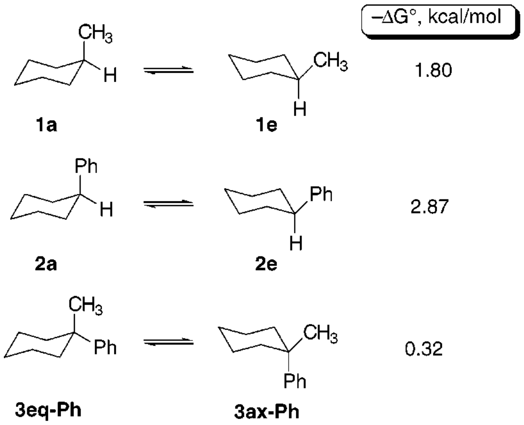
The structures and relative energies of the conformers of phenylcyclohexane, and 1-methyl-1-phenylcyclohexane have been calculated at theoretical levels including HF/6-31G*, B3LYP/6-311G*, MP2/6-311G*, MP2/6−311(2df,p), QCISD/6-311G*, and QCISD/6-311G(2df,p). The latter gives conformational enthalpy ($\Delta H°$), entropy ($\Delta S°$), and free energy ($\Delta G°$) values for phenylcyclohexane that are in excellent agreement with the experimental data. The calculations for 1-methyl-1-phenylcyclohexane find a free energy difference of 1.0 kcal/mol at −100 °C, favoring the conformation having an axial phenyl group, that is in only modest agreement with the experimental value of 0.32 ± 0.04 kcal/mol. The origin of the phenyl rotational profiles for the conformers of phenylcyclohexane and 1-methyl-1-phenylcyclohexane is discussed.

We recently reported the results of an experimental and computational investigation of the conformational behavior of methyl- (**1**), ethyl-, isopropyl-, and *tert*-butylcyclohexane.[2] As a continuation of this study, it was of interest to explore the ability of modern ab initio molecular orbital theory to account for the structures and relative energies of phenylcyclohexane (**2**) and 1-methyl-1-phenylcyclohexane (**3**).

The conformational free energy ($-\Delta G°$) of phenylcyclohexane (**2**) has been determined in a number of studies.[3,4] The currently accepted "best" value,[5] obtained by Eliel and Manoharan from a careful low-temperature ^{13}C NMR study of *cis*-4-methyl-1-phenylcyclohexane, is 2.87 ± 0.09 kcal/mol at −100 °C,[3] and a value of 2.7 ± 0.3 kcal/mol at 700 °C was estimated by Squillacote and Neth from the results of a high-temperature cryogenic trapping experiment for phenylcyclohexane.[6] In view of the fact that the conformational energy of methylcyclohexane (**1**) is 1.80 ± 0.02 kcal/mol,[2] it might be anticipated, assuming additivity of conformational energies, that 1-methyl-1-phenylcyclohexane (**3**) would preferentially adopt a conformation in which the phenyl group is in the equatorial position. In fact, as illustrated below, the conformation of **3** with axial phenyl (**3ax-Ph**) is favored by 0.32 ± 0.04 kcal/mol at −100 °C.[3,7]



While additivity of conformational energies is generally not to be expected for geminally disubstituted cyclohexanes,[5] the rather extreme example presented by 1-methyl-1-phenylcyclohexane (**3**) is a classic conformational problem that has been addressed in several studies.[3,8−10] In an elegant early application of molecular mechanics (MM1), Allinger and Tribble correctly predicted that the conformation of **3** having an axial phenyl (**3ax-Ph**) should be more stable than the alternative chair conformation (i.e., **3eq-Ph**), and they calculated an energy difference of 0.90 kcal/mol.[8] Subsequent MM2 calculations by Eliel's group reduced the calculated energy difference to 0.61 kcal/mol.[9] In each of these molecular mechanics studies, the nonadditivity of conformational energies observed for **3** was attributed to fact that the preferred rotameric conformation of an equatorial phenyl is severely perturbed by introduction of a geminal methyl group.[8,9] According to this analysis, the more stable rotational conformation of the axial phenyl group in **2a**, which has the phenyl perpendicular to the bisector plane of the cyclohexane ring, is not affected by the presence of the

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[2] Wiberg, K. B.; Hammer, J. D.; Castejon, H.; Bailey, W. F.; DeLeon, E. L.; Jarret, R. M. *J. Org. Chem*. **1999**, *64*, 2085.

[3] Eliel, E. L.; Manoharan, M. *J. Org. Chem*. **1981**, *46*, 1959.

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[6] Squillacote, M. E.; Neth, J. M. *J. Am. Chem. Soc.* **1978**, *109*, 198.

[7] A low temperature ^1H NMR study of 1-methyl-1-phenyl-4,4-dimethoxycyclohexane indicated a 0.34 kcal/mol preference for the conformation having axial phenyl. See: De Beule, H.; Tavernier, D.; Anteunis, M. *Tetrahedron* **1974**, *30*, 3573.

[8] Allinger, N. L.; Tribble, M. T. *Tetrahedron Lett.* **1971**, 3259.

[9] Hodgson, D. J.; Rychlewska, U.; Eliel, E. L.; Manoharan, M.; Knox, D. E.; Olefirowicz, E. M. *J. Org. Chem*. **1985**, *50*, 4838.

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geminal methyl group; conversely, the more stable rotational conformation of the equatorial phenyl group in **2e**, which has the plane of the phenyl in the symmetry plane of the cyclohexane chair, is strongly perturbed by the introduction of a geminal methyl group. It was of interest to compare these molecular mechanics results with ab initio data.

The objectives of this study were as follows: (a) to gain further information on the level of theory needed to reproduce conformational energies;[11] (b) to study the origin of the large conformational preference of the phenyl group in cyclohexane; and (c) to further explore the origin of the axial phenyl preference in 1-methyl-1-phenylcyclohexane.

Calculations

Initial geometry optimizations were carried out at the HF/6-31G* level, and zero-point energies, obtained at this level, were scaled by 0.893. In light of the fact that correction for electron correlation is often important in conformational studies, we have made use of several methods for calculating this correction. One approach involved density functional theory at the B3LYP/6-311G* level.[12] This makes use of a three-parameter functional that is a hybrid of exact (Hartree−Fock) exchange terms and gradient-corrected exchange and correlation terms, similar to those first suggested by Becke.[13] Geometry optimizations also were carried out using MP2/6-31G* followed by a MP2/6-311G* calculation using the above geometry, allowing a comparison with the B3LYP/6-311G* results.

In our study of the alkylcyclohexanes,[2] it was found that MP2 gave more satisfactory relative energies than did B3LYP, with the latter energies on one side of the experimental values and MP2 on the other side. The most satisfactory level was QCISD with fairly large basis sets. For this reason, the QCISD/6-311G* energies were calculated using the MP2/6-31G* geometries. In addition, the effect of additional polarization functions was examined at the MP2/6-311G(2df,p) level, allowing QCISD/6-311G(2df,p) energies to be estimated via eq 1.

$$\text{QCISD/6-311G(2df,p)} = \text{QCISD/6-311G*} + \text{MP2/6-311G(2df,p)} - \text{MP2/6-311G*} \quad (1)$$

This approach is based on the observation by Pople and co-workers that the effects of additional polarization functions are to a good approximation the same at the QCISD and MP2 levels of theory.[14] We anticipated that this theoretical level might best reproduce the experimental data.

Table 1. Calculated Energies for Phenylcyclohexane (2)

	conformer energies[a]		ΔE (kcal/mol)[b]
	ax-Ph	eq-Ph	
basis set			
HF/6-31G*	−463.746 03	−463.752 98	4.36
B3LYP/6-311G*	−467.019 13	−467.025 22	3.82
B3LYP/6-311G* rot. TS	−467.018 16	−467.020 51	
MP2/6-31G*	−465.292 75[c]	−465.297 34	2.88
MP2/6-31G* rot. TS	−465.290 73	−465.291 92	
MP2/6-311G*[d]	−465.453 95	−465.458 33	2.75
MP2/6-311G(2df,p)[d]	−465.806 20	−465.810 18	2.50
QCISD/6-311G*[d]	−465.544 93	−465.550 03	3.20
QCISD/6-311G(2df,p)[e]	−465.897 18	−465.901 88	2.95
energies (kcal/mol)			
Ph rotational barrier			
B3LYP/6-311G*	0.61	2.96	
MP2/6-31G*	1.27	3.40	
ZPE[f]	151.34	151.02	0.32
$(H°_{298} - H°_0)$	7.16	7.33	−0.16
$(G°_{298} - G°_0)$	−23.55	−23.08	−0.47
$S°$ (cal/mol-deg)	103.00	101.97	1.03

[a] Total energies are given in hartrees (H); other energies are in kcal/mol (1 H = 627.51 kcal/mol). [b] Axial-Ph − equatorial-Ph. [c] The torsional angle between the phenyl and C(1)−H is 65.9°. [d] Calculated using the MP2/6-31G* optimized geometries. [e] Estimated value, see text. [f] Zero point energies; HF/6-31G* frequencies were scaled by 0.893. The internal rotor modes were treated separately, and their zero-point energies are included.

Table 2. MP2/6-31G* Structural Data for Conformers of Phenylcyclohexane (2) and 1-Methyl-1-phenylcyclohexane (3) Shown in Figure 1 as Structures A−D

	conformer			
parameter	eq-Ph (**2**) A	ax-Ph (**2**) B	eq-Me-ax-Ph (**3**) C	ax-Me-eq-Ph (**3**) D
r(1-A)	1.509	1.525	1.530	1.529
r(1−2)	1.535	1.541	1.540	1.545
r(1−6)	1.535	1.537	1.529	1.539
r(2−3)	1.529	1.528	1.529	1.530
r(5−6)	1.529	1.532	1.529	1.531
r(3−4)	1.529	1.528	1.529	1.527
r(4−5)	1.529	1.528	1.529	1.527
∠(1−A−B)	120.7	123.3	121.6	119.3
∠(1−A−C)	121.0	119.2	121.1	123.2
∠(2−1 6)	110.3	108.5	106.5	108.2
∠(1−2−3)	111.4	111.8	112.6	113.8
∠(1−6−5)	111.4	113.2	112.8	113.7
∠(2−3−4)	111.2	110.6	110.8	111.2
∠(3−4−5)	111.2	110.8	111.2	111.1
∠(A−1−H(7))	107.5	106.5	107.7	107.7
∠(2−3−Ha)	109.2	109.4	108.4	110.2
∠(6−5−Ha)	109.2	110.2	109.6	110.6
τ(B−A−1−H(7))	0.0	110.0	89.2	63.1
τ(C−A−1−H(7))	180.0	−65.9	−84.5	−116.0
τ(6−1−2−3)	−55.8	−57.7	−63.6	−53.0
τ(1−2−3−4)	56.0	58.9	53.4	55.6
τ(2−3−4−5)	−55.6	−56.6	−52.3	−55.3
τ(3−4−5−6)	55.8	54.2	64.3	55.5
τ(4−5−6−1)	−56.0	−54.5	−57.4	−56.3
τ(5−6−1−2)	55.8	54.6	58.0	53.3

Phenylcyclohexane

The conformational isomers of phenylcyclohexane (**2a** and **2e**) were studied via geometry optimization at the HF/6-31G*, B3LYP/6-311G*, and MP2/6-31G* theoretical levels, and the results are summarized in Table 1. The optimizations were carried out with no symmetry restraints and with the phenyl ring initially twisted away from a symmetrical arrangement. MP2/6-311G*, MP2/6-311G(2df,p), and QCISD/6-311G* energies were obtained using the MP2/6-31G* structures.

At all levels of theory (Table 2), equatorial phenylcyclohexane (**2e**) was found to preferentially adopt a conformation in which the phenyl is eclipsed with the C(1)−H bond (termed the "parallel" conformation by Allinger and Tribble);[8] structural data for **2e** obtained from the MP2/6-31G* calculations are summarized in Table 2 and Figure 1 A. The lowest energy rotational arrangement of the phenyl group in the axial isomer (**2a**),

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(11) Previous ab initio studies of monosubstituted cyclohexanes have been reviewed and the difficulties attending such calculations have been discussed: see, Cremer, D.; Szabo, K. J. In *Conformational Behavior of Six-Membered Rings*; Juaristi, E., Ed.; VCH Publishers: New York, 1995; pp 59−135.

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(13) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(14) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

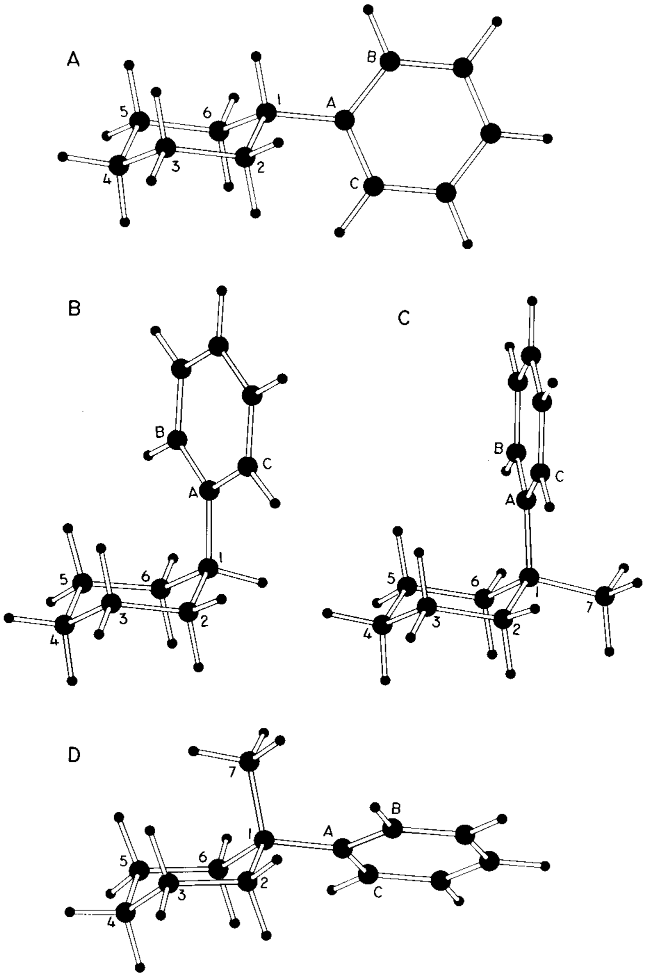

Figure 1. Minimum energy MP2/6-31G* structures for (A) eq phenylcyclohexane (**2e**), (B) ax phenylcyclohexane (**2a**), (C) ax-Ph-eq-Me 1-methyl-1-phenylcyclohexanes (**3ax-Ph**), and (D) eq-Ph-ax-Me 1-methyl-1-phenylcyclohexane (**3eq-Ph**).

obtained from the MP2/6-31G* calculations and illustrated in Figure 1B, is one in which the plane of the phenyl is rotated with respect to the bisector of the cyclohexane ring by about 24° (the calculated torsional angle is 65.9°); complete structural data for **2a** are summarized in Table 2. It should be noted that the symmetrical "phenyl-perpendicular" conformation of **2a** (torsional angle of 90°)[8] is less than 1 kcal/mol higher in energy than the minimum energy structure.

The calculated differences in energy (ΔE) between the axial and equatorial conformations of **2** are summarized in Table 1. At the B3LYP level, after correction for the difference in zero-point energies, the energy difference was 4.1 kcal/mol, and that calculated at MP2/6-311G* was 3.1 kcal/mol. The QCISD/6-311G* calculations led to an energy difference of 3.5 kcal/mol, and QCISD/6-311G(2df,p) gave 3.3 kcal/mol. Clearly, the B3LYP as well as the HF models lead to energy differences that are too large.

To correct the calculated energy differences to higher temperatures so that they may be directly compared with the experimental data, it is necessary to know the barrier to rotation of the phenyl group in both the axial (**2a**) and equatorial (**2e**) isomers. This aspect was explored at the theoretical levels noted above, giving the results summarized graphically in Figure 2. One might normally expect that the bond between a trigonal atom and a tetrahedral atom would have a small 6-fold rotational barrier, as is found with toluene, nitromethane and other similar compounds.[15] As illustrated in Figure 2, this is approximately the case for the axial conformer (**2a**) of phenylcyclohexane at the HF/6-31G* and B3LYP/6-311G* levels and also for the MM3 molecular mechanics procedure. However, the MP2/6-31G* result was considerably different in that it indicates a very broad minimum in the rotational energy profile between approximately 60° and 120°. As described below, the most satisfactory fit to the experimental free energy difference was obtained when the conformational entropy was evaluated using the rotational profile calculated at the MP2/6-31G* level. The potential energy change accompanying rotation of the phenyl group in equatorial phenylcyclohexane (**2e**) is also shown in Figure 2, and it can be seen that the ab initio and MM3 relative energies are in remarkably good agreement.

To compare the calculated energy difference (ΔE) between the axial and equatorial isomers of **2** (Table 1) to the experimentally determined conformational energy of phenylcyclohexane, ΔE must be corrected for the difference in zero-point energies between the two conformers, the change in ΔH° on going from 0 K to the higher temperatures at which the measurements were made (i.e., −100 and 700 °C) must be computed, and ΔH° must then be converted to ΔG° using the calculated entropy difference. This was done using the MP2/6-31G* rotational profiles and the QCISD/6-311G(2df,p) energy difference, giving the results shown in Table 3.[16] The rotational profiles were obtained via a set of calculations in which one torsional angle was constrained and all of the other degrees of freedom were allowed to relax. The energies and reduced moments of inertia were fit by Fourier series, the rotational energy levels were calculated, and from these data the rotational contribution was calculated.[17]

The calculated ΔG° at −100 °C, 2.9 kcal/mol, is in excellent accord with the experimental value of 2.87 ± 0.09 kcal/mol,[3] and that at 700 °C, 2.3 kcal/mol, is in satisfactory agreement with the experimental value of 2.7 ± 0.3 kcal/mol.[6] In this connection, it might be noted that the calculated conformational entropy difference (Table 3, $\Delta S^\circ = 1.0$ eu at 25 °C favoring **2a**), is considerably smaller than that obtained by Garbisch and coworkers from a study of the base-catalyzed equilibration of cis- and *trans*-4-*tert*-butyl-1-phenylcyclohexanes.[18]

Having demonstrated that the approach described above gives conformational energies that are in good agreement with available experimental data for phenylcyclohexane, it was of interest to explore the origin of the high rotational barrier calculated (Figure 2) for the equatorial isomer (**2e**). Allinger and Tribble have proposed that interaction of the ortho-hydrogens of an equatorial phenyl with the equatorial hydrogens at C(2,6) of the cyclohexane ring is responsible for the fairly high

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[15] For example, the barrier to rotation in toluene is a mere 13 cal/mol (Kreiner, W. A.; Rudolph, H. D.; Tan, B. T. *J. Mol. Spectrosc.* **1973**, *48*, 86) while the barrier in nitromethane is less than 6 cal/mol (Rohart, F. *J. Mol. Spectrosc.* **1975**, *57*, 301).

[16] Details of the thermal corrections are given in the Supporting Information.

[17] Murcko, M. A.; Castejon, H.; Wiberg, K. B. *J. Phys. Chem.* **1996**, *100*, 16162.

[18] Eliel has also noted (ref 3) that the conformational enthalpy reported by Garbisch and co-workers (ref 4c) for the **2a** → **2e** equilibrium ($\Delta S^\circ = 2.09 \pm 0.45$ eu) is most likely too large.

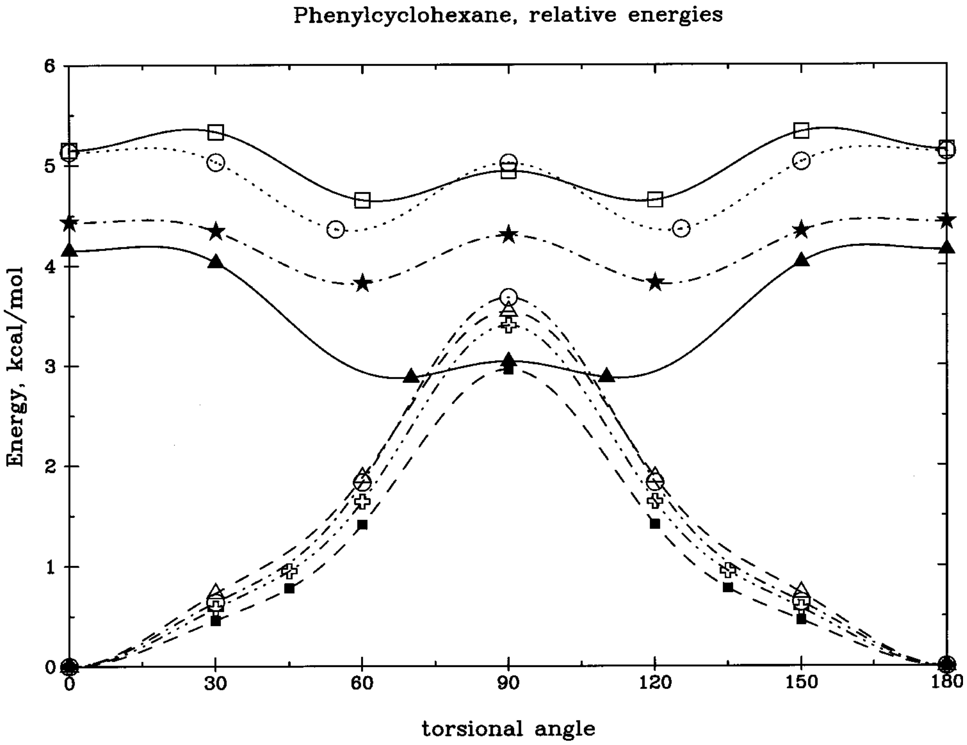

Figure 2. Potential energy change for rotation of the phenyl group in phenylcyclohexane; the torsional angle is defined by B−A−C(1)−H(1) of Figure 1A, B. The upper curves are for the axial conformer (**2a**), and the lower curves are for the equatorial conformer (**2e**). The legend is as follows: axial (**2a**) □ = MM3, O = HF/6-31G*, ★ = B3LYP/6-311G*, ▲ = MP2/6-31G*; equatorial (**2e**) Δ = MM3, O = HF/6-31G*, ■ = B3LYP/6-311G*, + = MP2/6-31G*.

Table 3. Calculated Conformational Enthalpy ($\Delta H°$), Entropy ($\Delta S°$), and Free Energy ($\Delta G°$) for Phenylcyclohexane (2) and 1-Methyl-1-phenylcyclohexane (3) Based on QCISD/6-311G(2df,p) Results

compd	T, °C	$-\Delta H°$, kcal/mol	$\Delta S°$, eu	$-\Delta G°$, kcal/mol
phenylcyclohexane (**2**)[a]	−100	3.2	−1.3	2.9
	25	3.1	−1.0	2.8
	700	2.8	−0.5	2.3
1-methyl-1-phenyl cyclohexane (**3**)[b]	−100	−1.3	1.4	−1.0
	25	−1.3	1.4	−0.8

[a] Data for ax-Ph → eq-Ph equilibrium of **2**; $-\Delta H°_0 = 3.3$ kcal/mol. [b] Data for ax-Ph-eq-Me → eq-Ph-ax-Me equilibrium of **3**; $-\Delta H°_0 = -1.2$ kcal/mol.

barrier to rotation about the phenyl−C(1) bond in **2e**.[8] As a result, the equatorial phenyl group preferentially adopts a conformation, shown in Figure 1 (**A**), in which the aromatic ring eclipses the C(1)−H bond. Additional insight into the factors responsible for the rotational barriers in each of the conformational isomers of **2** is provided by an analysis, summarized in Figure 3, of the principal short H···H nonbonded distances in various rotameric arrangements of the axial isomer (Figure 3A,B) and equatorial isomer (Figure 3C,D) of **2**. Clearly, only conformer D of the equatorial isomer, which is calculated to be the lowest energy isomer, is free from short nonbonded distances; the distance between the axial hydrogen at C(1) and the closest ortho hydrogen is 2.29 Å. It is also of interest to note that this structure has the shortest C−C bond (1.509 Å) between the two rings, a value that is typical for an sp^2−sp^3 bond. By way of comparison, the average C−C bond lengths in the cyclohexane ring are 1.531 Å, and the C−C bond lengths in the aromatic ring are 1.399 Å.

Rotation of the equatorial phenyl in **2e** by 90° leads to structure **C** (Figure 3) having two rather short H···H nonbonded distances. Similarly, in the axial phenyl isomer (**2a**), both the "phenyl-perpendicular" (Figure 3, **A**) and the "phenyl-parallel" (Figure 3, **B**) rotameric arrangements have short H···H contacts. In addition to the distances illustrated in Figure 3, conformer **B** of **2a** has an additional short nonbonded distance of 2.17 Å between the equatorial hydrogen at C(1) and the closest ortho hydrogen. In light of the fact that H···H nonbonded repulsion is negligible beyond about 2.4 Å but increases to about 1 kcal/mol at 2.0 Å,[19] these interactions nicely account for the relative stability of the equatorial phenyl-parallel rotamer (Figure 3D).

It should also be noted that the phenyl-perpendicular rotameric arrangements of both the axial and equatorial isomers (Figure 3A,C) have rather long C−C bonds between the rings. Whereas the H···H nonbonded interactions may be relieved by bending the C−H bonds, this is not so readily accomplished with the C−C bonds of cyclohexane because all of the bond angles are coupled. Thus, the long aryl−C(1) bonds in A and C are probably the result of C···C nonbonded repulsions between the C(2,6) carbons of the cyclohexane ring and the ortho carbons of the aromatic ring. Indeed, the C···C nonbonded interaction energy, which is negligible above about 3.3 Å, begins to rise quite rapidly at smaller distances.[20] Conformer A (Figure 3) of **2a** has ortho-carbons that are only 2.95 Å removed from the C(2,6) carbons of the cyclohexane ring, and in conformer C of **2e**, this distance is 2.94 Å. As a comparison, the distances in B and D are 3.25 and 3.13 Å, respectively.

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(19) Wiberg, K. B.; Murcko, M. A. *J. Comput. Chem.* **1987**, *8*, 1124.
(20) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.

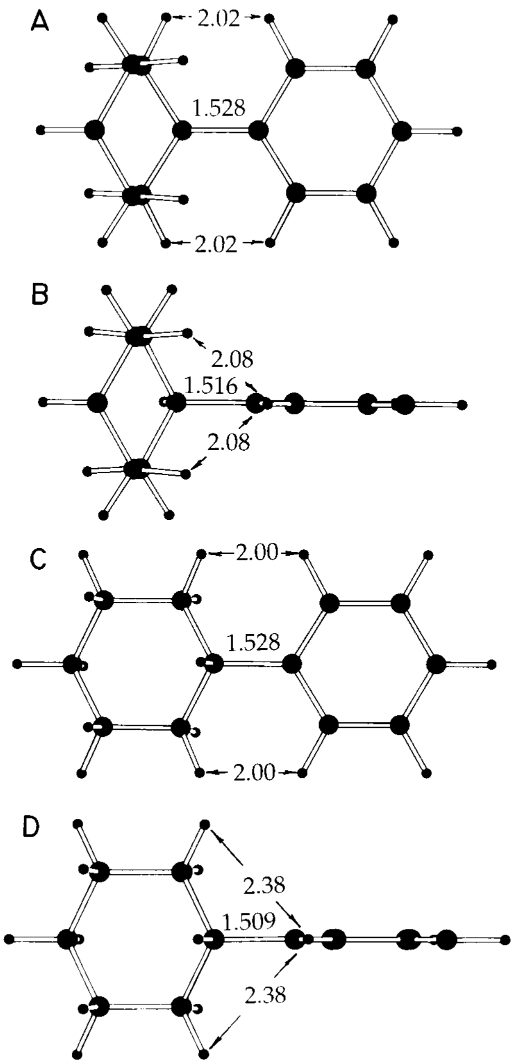

Figure 3. Nonbonded interactions in the "phenyl-parallel" and "phenyl-perpendicular" rotamers of axial and equatorial phenylcyclohexane: A and B are ax phenylcyclohexane (**2a**); C and D are eq phenylcyclohexane (**2e**).

1-Methyl-1-phenylcyclohexane

The conformational isomers of 1-methyl-1-phenylcyclohexane, **3**, were studied at the same theoretical levels as phenylcyclohexane giving the results summarized in Table 4 and illustrated in Figure 4. The MP2/6-311G*, MP2/6-311G(2df,p), and QCISD/6-311G* calculations were carried out using the MP2/6-31G* structures, and the vibrational frequencies, calculated at the HF/6-31G* level, were scaled by 0.893 to give estimates of the zero-point energies. The most stable structures of **3ax-Ph** and **3eq-Ph** are depicted in Figure 1 (C and D, respectively) and the structural parameters for these conformers, obtained from the MP2/6-31G* calculations, are summarized in Table 2.

The energy profiles for rotation of the phenyl group in each isomer of **3** (Figure 1C,D) were calculated at the theoretical levels noted above and they are compared with those derived from MM3 in Figure 4. In contrast to the phenylcyclohexane, in which the axial isomer (**2a**) has a relatively small barrier and the equatorial form (**2e**) has a larger 2-fold barrier, the isomer of **3** having an axial phenyl (**3ax-Ph**) is found to have a sizable 2-fold barrier while the alternative conformation (**3eq-Ph**) has a small, approximately 6-fold, barrier. Consequently, the low phenyl rotation barrier calculated for **3eq-Ph** results in an approximately 1.4 eu contribution to $\Delta S°$ favoring the conformation of **3** with an equatorial phenyl group.

Table 4. Calculated Energies for 1-Methyl-1-phenylcyclohexane (3)

	conformer energies[a]		ΔE (kcal/mol)[b]
	ax-Ph-eq-Me	eq-Ph-ax-Me	
basis set			
HF/6-31G*	−502.778 62	−502.777 79	−0.52
B3LYP/6-311G*	−506.252 06	−506.251 19	−0.55
MP2/6-31G*	−504.464 87	−504.462 01[c]	−1.78
MP2/6-311G*[d]	−504.641 49	−504.638 54	−1.85
MP2/6-311G(2df,p)[d]	−505.027 66	−505.024 86	−1.75
QCISD/6-311G*[d]	−504.741 06	−504.739 28	−1.12
QCISD/6-311G(2df,p)[e]	−505.127 23	−505.125 60	−1.02
energies (kcal/mol)			
ZPE[f]	168.16	168.33	−0.17
$(H°_{298} - H°_0)$	7.84	7.90	−0.06
$(G°_{298} - G°_0)$	−23.23	−23.59	0.36
$S°$ (cal/mol-deg)	104.19	105.62	−1.43

[a] Total energies are given in hartrees (H); other energies are in kcal/mol (1 H = 627.51 kcal/mol). [b] Ax-Ph-eq-Me conformation − eq-Ph-ax-Me conformation. [c] The torsional angle between the phenyl and the C(1)-Me is 63.1°. [d] Calculated using the MP2/6-31G* optimized geometries. [e] Estimated value, see text. [f] Zero point energies; HF/6-31G* frequencies were scaled by 0.893. The internal rotor modes were treated separately and their zero point energies are included.

Thermochemical correction of the calculated energy and entropy differences between the conformational isomers of **3** (Table 4) to allow comparison with experimental data was accomplished following the procedure described above for phenylcyclohexane.[16] The results of these calculations are summarized in Table 3. The conformational free energy calculated at a temperature of −100 °C, $\Delta G° = 1.0$ kcal/mol favoring the isomer having an axial phenyl (**3ax-Ph**), is significantly larger than the experimental value of 0.32 ± 0.04 kcal/mol determined at the same temperature.[3] However, as noted in our previous report,[2] the energy difference between conformational isomers is often phase dependent and, since the calculated $\Delta G°$ refers to the gas phase while the experimental value was determined in solution, this difference may account in part for the discrepancy.

An analysis of the origin of the difference in energy between the two conformational isomers of **3** requires some way in which to partition the total energy. One approach to this problem involves calculation of the energies involved in transferring substituents from **3** to cyclohexane as shown in Figure 5. This procedure was calibrated by first examining the reaction of 1,1-dimethylcyclohexane with cyclohexane since there are experimental data[21] with which the transfer energy may be compared.

As illustrated in Figure 5, the calculated energy change for reaction of 1,1-dimethylcyclohexane with cyclohexane to give two equatorial methylcyclohexanes is −0.9 kcal/mol, a value that is in good agreement with the experimental value of −1.3 ± 0.7 kcal/mol.[21] The more interesting reaction is the one in which one equatorial methylcyclohexane and one axial methylcyclohexane are formed, for here the methyl groups retain the orientation they had in the gem-dimethyl compound. In this case,

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(21) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center, Texas A&M University: College Station, TX, 1994; Vol. 1.

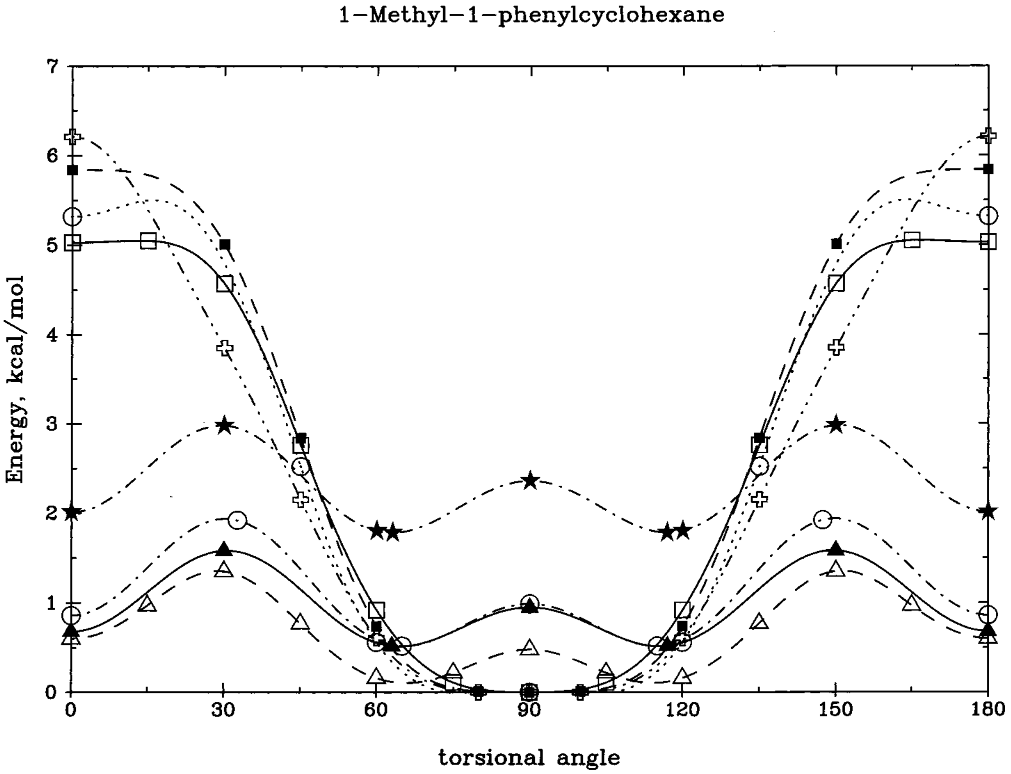

Figure 4. Potential energy change for rotation of the phenyl group in 1-methyl-1-phenylcyclohexane; the torsional angle is defined by B−A−C(1)−CH_3 of Figure 1C,D. The upper curves are for the phenyl-axial conformer (**3ax-Ph**), and the lower curves are for the phenyl-equatorial conformer (**3eq-Ph**). The legend is the same as for Figure 2.

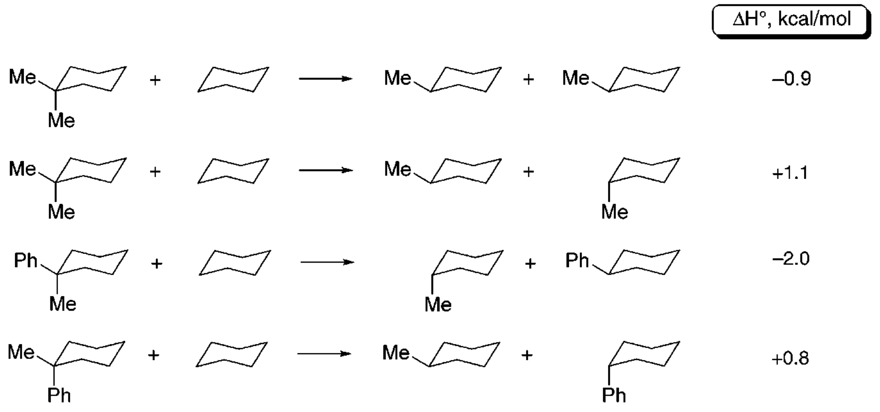

Figure 5. Isodesmic reaction energies.

the calculated energy change, +1.1 kcal/mol, indicates that the gem-disubstituted compound is stabilized with respect to the monomethyl cyclohexanes. The relative stability of the gem-dimethyl compound undoubtedly reflects the stabilization that is found in neopentane vis-à-vis the other pentane isomers.[22]

The reaction of each of the conformational isomers of 1-methyl-1-phenylcyclohexane (**3**) with cyclohexane was then examined. As show in Figure 5, reaction of **3eq-Ph** with cyclohexane to give axial methylcyclohexane and equatorial phenylcyclohexane (**2e**) is calculated to be exothermic by −2.0 kcal/mol; the analogous reaction of **3ax-Ph** with cyclohexane to give equatorial methylcyclohexane and axial phenylcyclohexane (**2a**) is endothermic by +0.8 kcal/mol. The latter value is close to that found for the transfer reaction of 1,1-dimethylcyclohexane with cyclohexane and it most likely reflects the stability derived from gem-substitution. Thus, there is apparently no destabilization of the axial phenyl group in **3ax-Ph** with respect to axial phenylcyclohexane.

The exothermic nature of the transfer reaction involving **3eq-Ph** suggests that this isomer is destabilized by about 3 kcal/mol (the difference in energy between this reaction and that involving **3ax-Ph**). The origin of this destabilization, as suggested by Allinger and Tribble,[8] is the presence of the *gem*-methyl in **3eq-Ph**. The preferred phenyl-parallel rotameric arrangement found in equatorial phenylcyclohexane (Figure 1, **A**), which avoids nonbonded interactions with the equatorial C(2,6) hydrogens, is no longer the lowest energy arrangement for an equatorial phenyl in **3**. Rather, **3eq-Ph** (Figure 1, **D**) preferentially adopts a conformation in which the phenyl is rotated by approximately 65° (Table 2) so as to avoid

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[22] Laidig, K. E. *J. Phys. Chem.* **1991**, *95*, 7709.

steric interaction with the C(1)-Me group. This analysis is consonant with the calculated rotational profile for equatorial phenylcyclohexane, shown in Figure 2, indicating an approximately 2 kcal/mol increase in energy when the equatorial phenyl is rotated by 65° from its preferred rotameric arrangement.

Calculations. The ab initio calculations were carried out using Gaussian-95,[23] and thermochemical corrections were made as previously described.[2]

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Supporting Information Available: Summary of the rotational barriers for phenylcyclohexane and 1-methyl-1-phenylcyclohexane and details of the thermal corrections. This material is available free of charge via the Internet at http://pubs.acs.org.

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