molecule lies astride an inversion center. A second molecule lies in general position. Since the thermal parameters relative to the latter C_6H_6 molecule refine to acceptable values by assuming atomic population parameters of 0.5, the ratio given above is confirmed to be correct. Rigid body models (D_{6h}) for all of the phenyl rings and the benzene molecule in general position were adopted during the least-squares refinement. The hydrogen atoms were introduced at calculated positions (C–H = 1.0 Å). Anisotropic thermal parameters were used only for the Rh, Se, P, and Cl atoms. The final difference Fourier map has the largest peak of 0.92 e/Å^3 which appears to be a rhodium ripple. Other peaks of about 0.5 e/Å^3 are observed in the solvent regions. Final coordinates of all the non-hydrogen atoms are reported in Table IV.

[(triphos)Rh(μ-C_2S_4)Rh(triphos)]$(BPh_4)_2 \cdot CH_2Cl_2$ (10)·CH_2Cl_2. The structure was solved by the Patterson method and Fourier techniques. During the least-squares analysis Rh, S, and P atoms as well as the unique carbon atom of the centrosymmetrically related C_2S_4 ligand were allotted anisotropic temperature factors. Also, the phenyl rings were treated as rigid bodies, and the hydrogen atoms were introduced at calculated positions. The non-hydrogen atoms of CH_2Cl_2 were assigned a population parameter of 0.5 and refined accordingly. A difference map showed some peaks (>1 e/Å^3) which were attributed to disorder in the dichloromethane solvent molecule. Also, one of the phenyl rings of the ligand triphos [one of those linked to the atom P(1)] is affected by some disorder as shown by the relatively high-temperature factors. Final coordinates of all non-hydrogen atoms are reported in Table V.

Computational Details. All calculations were of the extended Hückel type[43] using a modified version of the Wolfsberg–Helmholz formula.[44] The parameters for the rhodium atom were the same as in ref 45. Extensive use of Fragment Molecular Orbital analysis was performed.[46] The geometry of the model $[H_3Rh(\mu\text{-}C_2S_4)RhH_3]$ was fixed as follows: Rh–H = 1.7 Å; H–Rh–H = 90°; C–C = 1.4 Å; C–S = 1.7 Å; S–C–C = S–C–S = 90°.

Acknowledgment. We thank Dante Masi for technical assistance with X-ray analyses.

Supplementary Material Available: Anisotropic thermal parameters for compounds **4** and **10**·CH_2Cl_2 (4 pages); listing of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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A Simple High Energy Conformer Trapping Technique. Axial Phenylcyclohexane, NMR Spectra, and Thermodynamics

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Abstract: The axial conformer of phenylcyclohexane has been observed for the first time by using a unique but simple high-temperature cryogenic trapping technique. Thermodynamic and NMR spectral data have been obtained for this high-energy conformer, which is shown to have a perpendicular geometry. The NMR chemical shift differences between the equatorial and axial conformers are discussed in terms of their geometries and recent chemical shift theories.

Hassel first convincingly showed the existence of the two different positions of substitution on the chair form of a cyclohexane molecule.[1] He also recognized the preference of the equatorial position by any large group. However, the pioneering paper by Barton,[2] which pointed out the difference in chemical reactivity of these axial and equatorial substituents, catapulted these two conformers into the limelight of the chemical world. In fact, this discovery formed the cornerstone of the field of conformational analysis,[3] Since that time, the axial–equatorial conformational energy difference and the spectroscopic differences (especially NMR shifts) of the two conformers of a variety of functionalities have been of great interest to chemists.[4]

One of the most interesting substituents on a cyclohexane molecule is a phenyl ring. This group has generated discussion for a number of reasons. Axially disposed phenyl groups are known to exist in a number of natural products.[5] A phenyl substituent can adopt at least two different geometries in both the axial and equatorial positions.[6] The phenyl group is a simple substituent so knowledge of the NMR shift differences between the axial and equatorial conformers should offer insight into the controversy surrounding the origin of conformationally induced ^{13}C chemical shifts.[7-9] Finally, the phenyl group has been proposed as a ring locking group in preference to the *tert*-butyl since the latter has been shown to substantially distort the cyclohexane ring.[10] These reasons combine to make the phenyl group an important reference point in the cyclohexane system.

Unfortunately, studies on the phenyl substituent have been hampered by the large free energy difference between the axial and equatorial conformer (the *A* value). Though several estimates for this free energy have been made,[11-13] the methods chosen for these studies have necessarily been indirect. Molecules selected for these experiments contain substituents in addition to the

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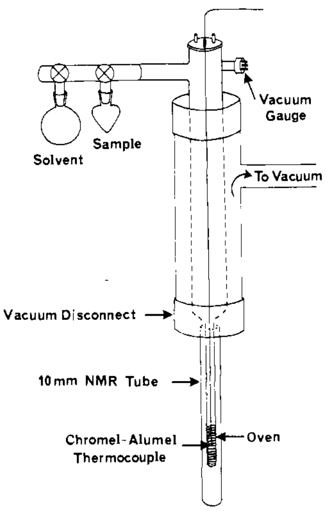

Figure 1. Schematic of trapping apparatus.

relevant phenyl group; thus it was assumed that the *A* value of the phenyl group could be obtained by subtracting the *A* value of the additional substituent from the overall $\Delta G°$ of the molecule. This counterpoise method is based on the assumption that the possible effects of the additional groups are negligible. In some cases[14] these effects have been shown to be important, thereby lending uncertainty to values obtained by the additive procedure. The extra substituent necessary for the counterpoise method also prevents straightforward determination of spectral shifts induced by the substituent of interest.

The most direct and unambiguous method of determining $\Delta G°$'s in monosubstituted cyclohexanes is by integration of the signals assigned to individual conformations in the NMR spectrum observed at low temperature, where ring inversion is quite slow.[15,16] This not only allows measurement of thermodynamic parameters but also gives valuable NMR spectral data for the individual conformers. However, molecules having a very one-sided conformational equilibrium (like phenylcyclohexane) have been difficult to study because the signal area of the minor form constitutes such a small percentage of the total, especially at the low temperature where the exchange rate is slow enough to allow observation of the resonances of both conformers. Therefore, the $\Delta G°$ and chemical shifts of axial phenylcyclohexane have not previously been measured directly. We have accomplished this by using a technique which allows a high temperature equilibrium to be established and subsequently trapped at −196 °C. This is a modified and much simpler procedure from that which was developed previously.[17] This method produces a sample which contains a significant amount of the previously unobservable higher energy conformer. This technique enables us to easily obtain rates of decay and ^{13}C and ^{1}H NMR spectral data of the metastable conformer. Since the high-temperature equilibrium is trapped efficiently, equilibrium constants can be obtained at a variety of temperatures.

Experimental Section

Phenylcyclohexane was obtained from Aldrich and used without further purification. Propane-d_1 was prepared by reacting *n*-propyl bromide with $Li(CH_3CH_2)_3BD$ in THF (1:1 molar ratio). The $CH_3CH_2CH_2D$ produced was trapped at −78 °C and was distilled several times to eliminate residual THF. Propane-d_8 was similarly prepared by reacting the tosylate of isopropyl alcohol-d_8 with $Li(CH_3CH_2)_3BD$.

Low temperature (−160 °C) ^{13}C and ^{1}H NMR spectra were recorded on a Bruker WM250 spectrometer operating at 62.89 MHz, while ^{1}H NMR spectra were recorded on a Bruker AM400 WB spectrometer operating at 400.13 MHz. We obtained ratios of the axial and equatorial conformers by integration of the ^{1}H spectra of conformational mixtures and by using dual display software to superimpose axial and equatorial resonances of the paired carbons. As pointed out by Booth and Jozefowicz,[18] at low temperatures the short T_1's of hydrogen bearing carbons implies that the relative areas of the peaks should be proportional to concentration. This is especially true in our study since we are at extremely low temperatures, and because we obtain our equilibrium constants by measuring the ratios between the very similar carbons which are paired in the axial–equatorial exchange.

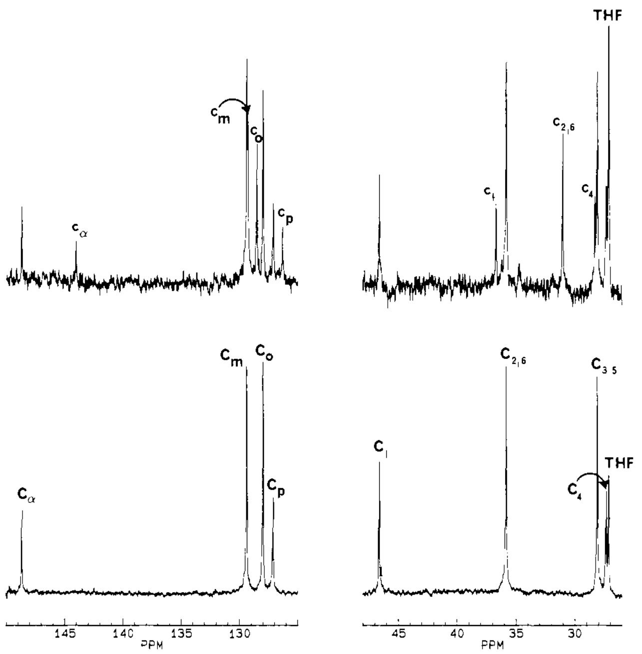

Figure 2. Top: ^{13}C NMR spectra of a trapped conformational mixture of axial and equatorial phenylcyclohexane at −160 °C in propane-d_1. The axial form resonances are assigned. Bottom: Same sample warmed to −120 °C and recooled. The equatorial resonances are assigned.

Samples were prepared (Figure 1) by passing phenylcyclohexane vapor through a variable temperature oven, composed of a quartz tube (3 mm i.d.) tightly wrapped over the last 4 cm with tantalum resistance wire. A chromel–alumel thermocouple was positioned inside the quartz tube about 2 cm from the tip, allowing temperature measurements at the center of the hot zone to be made. A 10-mm NMR tube was connected to the vacuum system by a quick vacuum disconnect and positioned around the oven, placing the bottom of the NMR tube about 2 cm from the tip of the oven. The NMR tube was cooled to −196 °C by immersion in liquid N_2. Even with the oven at 750 °C the temperature of the NMR tube were deposition occurred was measured to be very close to the temperature of liquid N_2. The pressure at the oven terminus was kept below 2×10^{-5} torr.

The high temperature equilibrium established in the hot oven (10 ms contact time) was then trapped as the molecules left the oven and impinged onto the surface of the cold NMR tube. For ^{13}C samples about 11 mg of degassed phenylcyclohexane was passed through the oven at 700 °C followed by subsequent slow vapor deposition of degassed propane-d_1 solvent onto the surface of the NMR tube which was kept at −196 °C. The NMR tube was sealed under vacuum and stored in liquid N_2. ^{1}H samples were prepared similarly; however, propane-d_8 was used as the solvent, and the amount of samples was varied between 1 and 12 mg. The deuterated propanes we used remained liquid for long periods of time when stored at −196 °C.

Results

By using the cryogenic trapping method described above, we are able to report the low-temperature ^{13}C spectra of the axial and equatorial conformers of phenylcyclohexane. The ^{13}C NMR spectrum at −160 °C of a deposition of phenylcyclohexane from an oven temperature of 700 °C is shown in Figure 2. Two sets of signals are observed, one of which corresponds to equatorial

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Table I. ^{13}C Chemical Shifts of Axial and Equatorial Phenylcyclohexane^a

phenylcyclohexane carbons	equatrl form chem shifts	axial form chem shifts	shift differncs
C_1	46.6	36.7	-9.9
$C_{2,6}$	35.8	31.0	-4.8
$C_{3,5}$	28.1	22.6	-5.5
C_4	27.3	28.3	+1.0
C_α	148.6	143.9	-4.7
C_{ortho}	127.9	128.4	+0.5
C_{meta}	129.3	129.2	-0.1
C_{para}	127.0	126.2	-0.8

^{a}Chemical shifts were measured in propane-d_1 at −160 °C, relative to the THF resonance at 68.4 ppm. Axial ortho and meta carbon assignments may be interchanged.

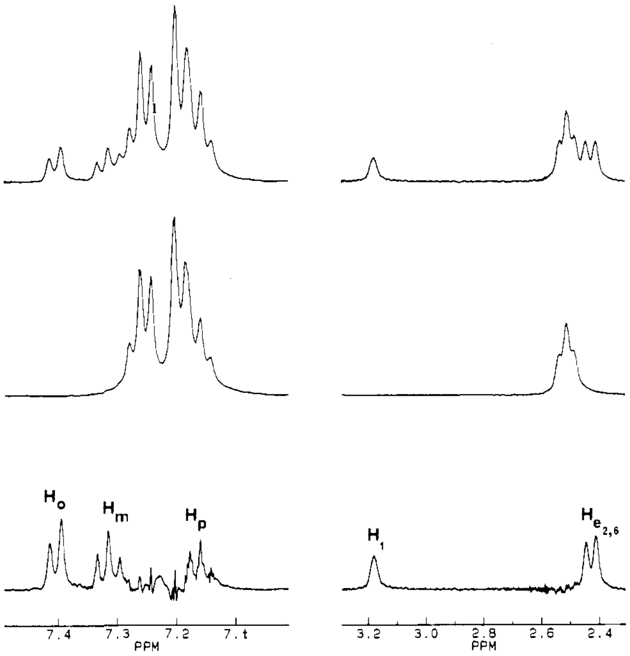

Figure 3. Top: ^{1}H NMR spectrum of a trapped conformational mixture of axial and equatorial phenylcyclohexane at −160 °C in propane-d_8. Middle: Same sample warmed to −120 °C and recooled leaving only equatorial form resonances. Bottom: ^{1}H spectrum of axial phenylcyclohexane obtained from subtraction of trapped and decayed spectra. Axial form resonances are assigned.

phenylcyclohexane.[13] When the solution is warmed to −120 °C the additional signals rapidly disappear with a concomitant increase in the intensities of the equatorial conformer's signals (Figure 2). The spectrum of the warmed solution at −160 °C is essentially identical with that obtained from a solution of phenylcyclohexane in propane-d_1; consequently, we have assigned the additional signals to axial phenylcyclohexane. ^{13}C chemical shifts for both conformations are recorded in Table I. Assignments of the equatorial conformer have been previously reported,[13] while those of the axial conformer were made by analogy with methylcyclohexane[16,19] and by comparison of relative intensities. Absent from Figure 2 is the axial $C_{3,5}$ signal, as it is situated on the side of the very large propane-d_1 solvent peak. The low-temperature ^{1}H spectrum was also obtained, and again signals were detected which were not present in an ordinarily prepared solution of phenylcyclohexane in propane. These signals decayed at −120 °C yielding a spectrum identical with that of equatorial phenylcyclohexane. Portions of the ^{1}H spectrum of this metastable species, which is undoubtly the axial conformer, could be obtained by subtraction of the deposited sample spectrum before and after warming (Figure 3).

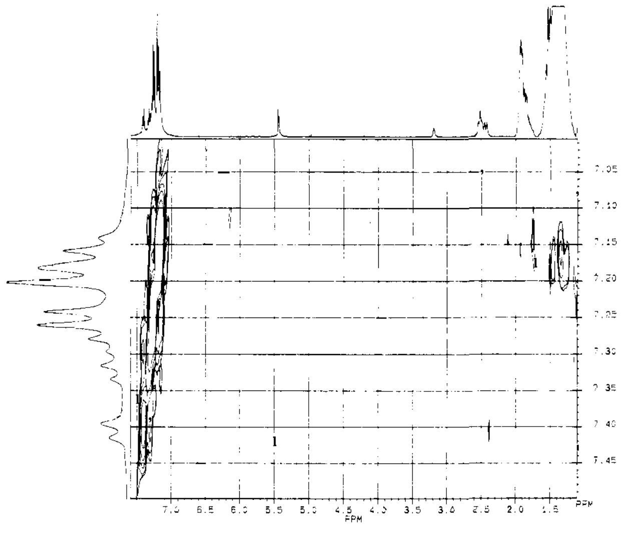

Figure 4. 2D ^{1}H–^{1}H NOESY contour plot of trapped conformational mixture of axial and equatorial phenylcyclohexane at −160 °C in propane-d_8. The cross peak at 6.2/7.12 ppm is due to a quad image of the large propane-d_8 solvent peak. The large resonances at 1.3 and 5.4 ppm are due to the CHD group of propane-d_8 and propene impurity in the propane-d_8, respectively.

Resonances of the axial conformer's ortho (7.40 ppm, $J_{o,m}$ = 7.7 Hz) meta (7.3 ppm), para (7.15 ppm, $J_{p,m}$ = 7.1 Hz), H_1 (3.16 ppm), and equatorial $H_{2,6}$ (2.42 ppm, J_{gem} = 13.3 Hz) protons were readily observed. These protons can be very nicely identified by the shifts and couplings which occur in the axial conformer. Upon going from the equatorial to the axial conformer the methine proton (a broad multiplet) is shifted downfield 0.7 ppm. The doublet at 2.42 ppm can be assigned to the 2,6-equatorial hydrogens since they show only a geminal coupling and no strong trans coupling as would be expected if this resonance represented axial protons. A major change in the shift of the ortho hydrogens eliminates masking of the aromatic resonances in the axial form and creates a situation which allows ready identification of the aromatic protons. The ortho hydrogens are shifted downfield 0.25 ppm and appear as a doublet from their ortho coupling to the meta protons. The triplets of the meta and para protons are readily distinguishable from their relative intensities. The other axial resonances were obscured by solvent or equatorial form peaks.

A 2D ^{1}H–^{1}H NOESY experiment was conducted on a trapped conformational mixture over an 18-h period at −160 °C (Figure 4). The cross peak at 2.4/7.4 ppm indicates a dipole–dipole relaxation mechanism between the ortho and 2,6-equatorial hydrogens of the axial conformer and implies a proximal spatial arrangement of these atoms. Other cross peaks were identical with those found for the equatorial form from a room temperature NOESY experiment or were due to relaxation via protio impurities of the propane-d_8 solvent. An additional cross peak at 6.7/7.12 ppm is derived from a quad image of the solvent peaks.

It has been shown previously that complete trapping of the high-temperature equilibrium is achieved with this technique.[20] Thus the $\Delta G°$ between the axial and equatorial conformers at 700 °C could be obtained by measuring the ratios of appropriate signals in the trapped low-temperature spectrum. Unfortunately, what appears to be preferential solubility of the axial conformer leads to spuriously large axial–equatorial ratios (Figure 2). Differential solubility of axial and equatorial conformers has been previously observed.[21] When 4 mg, rather than 1 mg, of sample are deposited from 700 °C the ratio of axial and equatorial conformers increases by a factor of 1.8. When 12 mg are used, much more axial form is apparent; the conformer ratio increases to 5.2 over that obtained for a 1-mg sample. Warming of the 12- and 4-mg samples caused substantially more material to go into solution. Thus unless extreme care is taken to dissolve all the phenylcyclohexane from

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the side of the tube, inaccurate ΔG°'s will result. However, when all phenylcyclohexane is allowed to solubilize a K_{eq} of 0.22 is measured and is equivalent to a ΔG° of 2.7 kcal/mol. This may be compared with the value of 2.0–3.1 kcal/mol reported in the literature,[11-13] but because of the differential solubility of the conformers and possible partitioning upon trapping of twist-boat conformers created in the oven to preferentially either the axial or equatorial form, we estimate an error of 10% in our ΔG° value.

We have also obtained the previously unreported value for the $\Delta G^\ddagger$ of the axial–equatorial decay process. The decay rate of the axial form was monitored at −154 °C and corresponded to a $\Delta G^\ddagger$ of 8.8 ± 0.1 kcal/mol, with most of the error being due to uncertainty in the temperature measurement. With a free energy of activation of this magnitude we see no decay at −160 °C, the temperature at which most of our spectra were recorded.

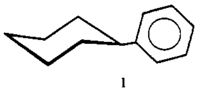
Discussion

If the conformational and spectral characteristics of simple models such as phenylcyclohexane are to be applied successfully to the study of more complex systems, the elucidation of structural and thermodynamic parameters of both equatorial and axial conformers of these simple systems must be achieved. Since the traditional use of 1,4-disubstituted derivatives may suffer from the assumption of additivity of conformational free energies for the two substituents[14] and prevents straightforward determination of spectral parameters, one would prefer to have a direct measure of the spectral and thermodynamic information for a given functionality in the **simple** *monosubstituted* cyclohexane. The importance and utility of the trapping technique used in this study is thus evident, since it has enabled us to directly obtain spectral and thermodynamic data of a previously unobservable molecule.

The cryogenic trapping of a high-temperature equilibrium mixture of equatorial and axial phenylcyclohexane yielded the low-temperature ^{13}C and ^{1}H NMR spectra of both conformers, from which we obtained a value of 2.7 kcal/mol for ΔG°. While our determination is disturbed by differential solubility of the conformers and possible differential decay of twist-boat forms produced in the oven, this is the first observation of an axial conformer of a monosubstituted cyclohexane with a ΔG° value of a magnitude which precludes any chance of observation of room or low-temperature equilibrium mixtures. Our value compares favorably to literature values obtained at low temperature, implying a small ΔS° between the two conformers since ΔG° does not change substantially over an 800 °C range. This result is substantially different from a large ΔS° reported in some elegant work on 2-phenyl-1,3-dioxane.[22] However, in our case the $H_{2,6}$–H_{ortho} interaction will substantially hinder rotation of the equatorial phenyl group, and free rotation, as is the case in the 1,3-dioxane, will not occur.

The rate of decay of the minor axial form was determined by measurement of the half-life at −154 °C and yielded a free energy of activation ($\Delta G^\ddagger$) of 8.8 ± 0.1 kcal/mol for the conversion of the minor to the major conformer. This compares to a value of 10.4 kcal/mol for methylcyclohexane.[23] The smaller value for the phenyl is reasonable since the transition state for ring inversion should have less steric interaction and be of similar energy for phenyl and methyl while the axial conformer should show the full strain associated with a 1,3-interaction.

Force field calculations[6] have suggested that the preferred conformation of equatorial phenylcyclohexane is with the plane of the phenyl ring parallel to the symmetry plane of the cyclohexane ring (I). For axial phenyl, this conformation (II) was shown to involve substantial steric interaction with the syn-axial hydrogens. Therefore, the conformation in which the phenyl is perpendicular to the cyclohexane symmetry plane (III) was calculated to be preferred. To date however, no experimental proof of the geometry of the axial phenyl group in fluid solution has been obtained.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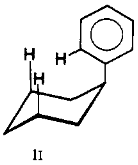

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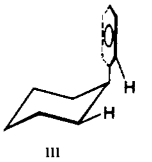

III

Examination of the literature does reveal a few X-ray crystal structures of molecules with axially disposed phenyl groups on cyclohexane rings. Of the four molecules, three exhibited the perpendicular phenyl orientation (III) while the fourth adopted a parallel phenyl geometry (II). The geometry adopted by these molecules seems to be controlled by the H_{ortho}–$H_{2,6}$ interaction. 1-(1-phenylcyclohexyl)piperidine hydrochloride[24] and *cis*-1-(*p*-bromophenyl)-*tert*-butylcyclohexane[25] adopt the perpendicular orientation (III) predicted by Allinger. However, inspection of these two structures shows that the phenyl avoids some H_{ortho}–$H_{2,6}$ interaction by rotating slightly about the C_1C_α bond. The importance of this interaction can be seen by the fact that *cis*-2-phenyl-5-*tert*-butyl-1,3-dioxane[26] assumes the perfectly perpendicular orientation. Here the H_{ortho}–O lone pair interaction must be substantially smaller than the H_{ortho}–$H_{2,6}$ interaction present in the previous two compounds. Additional dramatic evidence for the importance of this interaction is evidenced by the structure 1(e),2(e),3(e),4(e),5(e),6(e)-hexachloro-1(a)-phenylcyclohexane[27] which actually adopts the parallel axial geometry. Though the parallel phenyl configuration in this molecule introduces a steric interaction between the ortho hydrogen and the axial 3,5-hydrogens, the strain induced must be less than that produced by the interaction of the ortho hydrogens and the large chlorine atoms which would occur in the perpendicular geometry.

Because the axial phenyl conformer has not been previously observed, there is no actual evidence revealing which phenyl configuration this conformer adopts in the parent compound phenylcyclohexane. The X-ray data clearly illustrated that there was a difference in rotational attitude of the phenyl ring, depending on its environment, but of course the geometries found in these studies may be different from those adopted in fluid solution. We felt that the geometry of axial phenylcyclohexane could be determined from spectral data we had obtained, since it is well-known that differences in steric environment have a marked and predictable effect on chemical shifts and intranuclear relaxation.

Sterically hindered protons have downfield shifts.[28] Axial phenylcyclohexane, energetically unfavorable for just such H–H interactions, would therefore be expected to exhibit large proton steric effects which would be very conformationally dependent. The two possible axial conformers, parallel and perpendicular, should show quite different proton spectra. In both conformers, the methine hydrogen should show the observed 0.7 ppm downfield shift expected in a transition from an axial to an equatorial position. In the parallel orientation there would be no H_{ortho}–$H_{2,6}$ steric interaction, so no or perhaps only a small ring current induced downfield shift of the 2,6-protons would be predicted. In fact the 2,6-hydrogens have a very large downfield shift of almost 0.5 ppm. A shift of this size can only be explained by a very large preference for the perpendicular structure. The 0.2 ppm downfield shift of the ortho proton is also clearly due to the increase in steric hindrance present in the perpendicular conformation. Thus the ^{1}H chemical shifts imply that axial phenylcyclohexane adopts this perpendicular conformation.

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The low-temperature ^1H–^1H NOESY experiment provides definitive proof that the perpendicular geometry is adopted in fluid solution. In the perpendicular conformation the spatial proximity of the axial conformer's ortho and 2,6-equatorial protons would produce a strong dipole–dipole relaxation mechanism between these two nuclei, and a large cross peak between these two resonances in the NOESY spectrum would be expected. The parallel configuration would produce a large cross peak between the ortho and 3,5-protons for the same reason. Because the axial form ortho hydrogens at 7.4 ppm are substantially separated from the rest of the aromatic protons, the ^1H–^1H NOESY spectrum, should clearly establish which configuration is adopted. Indeed, the contour plot of a ^1H–^1H NOESY spectrum of a trapped mixture at −160 °C (Figure 4) shows a strong cross peak for the axial ortho protons at 2.4 ppm, the chemical shift of the equatorial 2,6-protons of the axial conformer. No cross peak was observed for the 3,5-axial hydrogens. This clearly shows that a **perpendicular phenyl configuration is adopted by the axial conformer of phenylcyclohexane.**

^{13}C shifts are also known to be dependent upon geometry. A steric polarization model had for some time been generally accepted as the source of these usually shielding chemical shift changes;[20] however, in recent years there have been a variety of alternative explanations. Bond angle changes,[8] specific orbital overlap,[6b] electric field effects.[30,31] and intrinsic deshielding of β-hydrogens[7] have all been used to explain the conformational dependence of carbon shifts. The axial–equatorial ^{13}C shift differences we have obtained with our trapping technique are not interfered with by effects of extra substituents. Thus we have a unique opportunity to gain information concerning the origins of these conformationally induced shifts and to further substantiate the geometry of the axial conformer of phenylcyclohexane.

In a perpendicular geometry the steric polarization model would predict a substantial upfield shift of the 2,6-carbon resonance. This would be accompanied by a concomitant upfield shift of the ortho resonance. The observed $C_{2,6}$ shift difference is in fact upfield by 4.8 ppm, supporting the perpendicular structure established by the ^1H spectra. However this shift is only 1.2 ppm larger than the shift difference in methylcyclohexane,[19] where there is no severe steric interaction at 2,6-carbons. Furthermore, the ortho carbons show a **downfield** shift of at least 0.5 ppm and perhaps 1.3 ppm if the axial ortho and meta carbon shift assignments are interchanged. Thus a **steric polarization effect cannot be the major contributer to the shift changes of these carbons.**

It has been suggested that the upfield shift of the 2,6-carbon resonance for axial conformers is due to a widening of the $C_1C_2C_3$ bond angle caused by steric interactions of the axial substituent.[8,31] If bond angle widening is the major cause of the isomeric shift difference of these carbons, then the fact that this difference is only 1.2 ppm larger for a phenyl as compared with a methyl substituent suggests that these two groups have relatively the same effect on this angle even though the phenyl group is substantially larger. Thus the insensitivity to substituent size of the axial-equatorial isomeric shift difference may indicate that the $C_1C_2C_3$ bond angle is relatively stiff. The isomeric shift of the ortho carbon is very unusual and must involve more than one shift effect, especially considering that the para carbon shifts in the opposite direction.

Perhaps the most interesting ^{13}C resonance in the spectrum of phenylcyclohexane is the very large isomeric shift of the C_1 carbon. An upfield shift almost 5 ppm larger than the corresponding shift in methylcyclohexane is evident. Any effect involving torsional angles or anomeric effect from axial 2,6-C–H bonds[32] would presumably influence not only the C_1 carbon but also other ring carbons. However the isomeric shifts of the other ring carbons are not as unusual as the C_1 shift when compared to the isomeric shifts in methylcyclohexane. Thus, we are left to conclude that the phenyl group in phenylcyclohexane induces a major geometric distortion which is localized on the C_1 carbon. In order to examine this situation more fully, we investigated this system with an MMII force field calculation.[33]

An MMII calculation was conducted for phenylcyclohexane and yielded a calculated energy difference between the preferred conformations of the axial and equatorial phenyl of 3.41 kcal/mol. As suggested by the X-ray data, the calculated minimum energy axial phenylcyclohexane structure is a skewed perpendicular structure[34] rotated about the C_1C_α bond by about 26°. The symmetric structure was calculated to be only slightly higher in energy, with an energy difference of 3.59 kcal/mol. A major change upon going from the equatorial to the axial conformer is a bending of the phenyl ring substantially back away from the cyclohexane ring by 14°, as compared to the angle adopted by an axial hydrogen. The $C_1C_2C_3$ bond angle changes very little in the two conformers, so the nonbonded strain is relieved mostly by the phenyl bending away rather that by flattening of the cyclohexane ring. The MMII structure supports the idea that most deformation caused by the axial phenyl is localized on the C_1 carbon as is evidenced by the ^{13}C chemical shift of that carbon and by the fact that the isomeric shift of the 2,6-carbons is similar to that of methylcyclohexane. A very recent MMII calculation for substituted phenylcyclohexanes confirms this result.[35] Further support for this localization of strain energy is found in work on 2-phenyl-1,3-dioxanes.[36] Here the dipole moment of the axial conformer could be explained by a bending away of the phenyl group with little or no other structural changes in the dioxane ring system. The involvement of bond angle changes in the isomeric shift of C_1 carbons has been discounted in a study of a series of monosubstituted cyclohexanes; however, the substituents used in this investigation had a very wide range of electronegativity. Anomeric type orbital interactions could easily interfere with the conclusions reached. It is, in any case, difficult to understand why bond angle changes would effect the 2,6-carbon shifts but not shifts at C_1 as is claimed by these authors.[30,31] We believe that the effect of bond angle changes on ^{13}C chemical shifts warrants reevaluation. However, the dependence of chemical shift changes with bond angle does not appear to be the same for $C_{2,6}$ and C_1 implying that other effects must also be operating in determining the geometry dependence of ^{13}C chemical shifts.

Conclusion

The simplified thermal trapping technique used in this study has been shown to be useful in easily obtaining thermodynamic and kinetic data of very high energy conformers. Specifically we find that axial phenylcyclohexane is 2.7 kcal/mol higher in energy than the equatorial conformer and is separated from it by an 8.8 kcal/mol barrier. Furthermore, the spectral data can be used to define the geometry of this previously unobserved conformer. We find that axial phenylcyclohexane adopts the perpendicular configuration and that the molecule accomplishes a substantial relief in steric strain by distortion primarily at the C_1 carbon rather than by flattening the entire ring system. Our ^{13}C spectral data also suggest that the steric polarization model for conformationally induced changes in ^{13}C chemical shifts is not adequate and that bond angle changes may play an important role in these shift changes.

Registry No. $CH_3CH_2CH_2D$, 20717-73-1; phenylcyclohexane, 827-52-1; *n*-propyl bromide, 106-94-5; propane-d_8, 2875-94-7; isopropyl alcohol-d_8, 22739-76-0.

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