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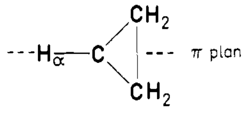
A Proton Magnetic Resonance Investigation of the Preferred Conformation and the Barrier to Internal Rotation of Phenylcyclopropane

William J. E. Parr[1] and Ted Schaefer*

Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Manitoba, Canada R3T 2N2. *Received September 8, 1976*

Abstract: Analysis of the proton magnetic resonance spectrum of phenylcyclopropane in CS$_2$ solution yields -0.23 ± 0.02 Hz for the spin-spin coupling constant over six bonds between the para proton in the phenyl group and the α proton in the cyclopropyl moiety. The assumption that this coupling is dominated by a σ-π electron mechanism, combined with a hindered rotor treatment, indicates a barrier to internal rotation about the C-C bond of 2.0 ± 0.3 kcal/mol. This value assumes a predominantly twofold barrier and implies that the low-energy conformation is that in which the C-H$_\alpha$ bond prefers the plane of the phenyl group. The result is compared with theoretical and other experimental data. The phenyl proton chemical shifts are consistent with electron donation from cyclopropyl to phenyl.

The Walsh model[2] of the orbitals in cyclopropane suggests that maximum conjugative interaction between pπ orbitals of the substituent and the pseudo-π orbitals of the cyclopropyl group in cyclopropane derivatives occurs for a conformation, **1**, in which the C-H$_\alpha$ bond of the cyclopropyl group lies in the benzene plane. If the conformation of the cyclopropyl derivative is determined by this conjugation, then **1** will be of lower energy than **2** and the barrier to internal rotation may well be predominantly twofold in nature.



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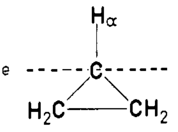

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The model is consistent with experiment[3-5] in that the π planes of the NO$_2$, CHO, COF, and COCl groups in the corresponding derivatives of cyclopropane do prefer an orientation corresponding to **1**. Furthermore, the twofold component in the barrier to internal rotation is 3.3 ± 1.5 kcal/mol for the nitro compound[3] and is 4.4 ± 0.4 kcal/mol in the aldehyde.[4]

Measurements[6] of the temperature dependence of the chemical shift between the ortho and meta protons in *p*-deuteriophenylcyclopropane suggest that **1** is 1.4 kcal/mol lower in energy than **2**, although no error limits were assigned. The torsion frequencies[7] indicate a barrier of 5.8 kcal/mol but the same method yielded rather large internal barriers in molecules like biphenyl and stilbene.

Classical calculations[8] of the conformational energies of **1** and **2** gave ambiguous results. The electron diffraction pattern[8] was consistent with a preferred conformation **1**.

On the other hand, dipole moment[9] and infrared intensity data[10] are interpreted to mean that the cyclopropyl group behaves like an alkyl group in donating electrons to the aromatic ring, its Hammet σ constant being near -0.1.

In this paper an analysis of the proton magnetic resonance spectrum of phenylcyclopropane in CS$_2$ solution yields long-range coupling constants between the ring protons and α proton on the cyclopropyl group. The assumption of a predominantly twofold barrier to internal rotation allows the deduction of its magnitude from the long-range coupling. Semiempirical and ab initio molecular orbital calculations are presented for **1** and **2**. The ring proton chemical shifts are compared with those expected in toluene.

Experimental Section

A 10 mol % solution of phenylcyclopropane (Aldrich, 97%) in CS$_2$, containing a little tetramethylsilane, was degassed by the freeze-pump-thaw technique. The proton magnetic resonance spectrum was calibrated at 305K in the frequency sweep mode on an HA100 spectrometer.

INDO MO FPT calculations[11] were performed for conformations **1** and **2** using the geometry based on the electron diffraction data. Ab initio minimal basis set molecular orbital calculations at the STO-3G level[12] were also performed on an IBM 370/158 system.

Results and Discussion

Spectral Analysis. The spectrum corresponds to an ABB′-CC′RXX′YY′ spin system (see **3**) and, as such,[13] cannot be

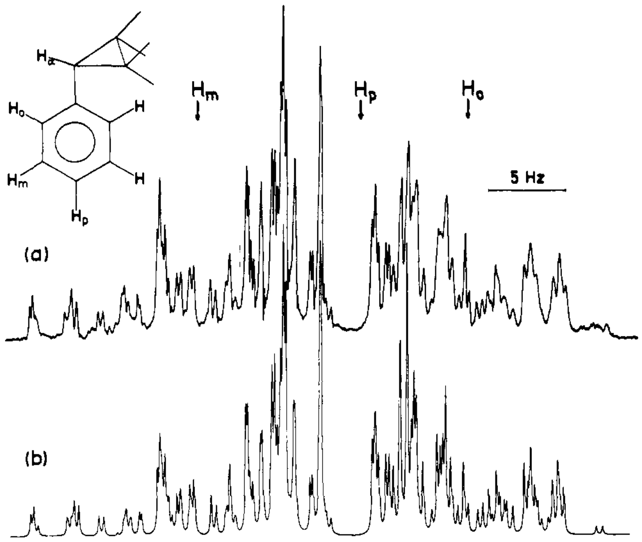


Figure 1. The observed phenyl proton magnetic resonance spectrum at 100 MHz and 305 K of a 10 mol % solution in CS_2 is shown in a. The calculated spectrum is displayed in b. The original spectra were recorded at 1 Hz/cm. Note the broadening of the ortho protons caused by unresolved coupling to the β protons of the cyclopropyl group. The presence of small amounts of impurities is evident in the experimental spectrum.

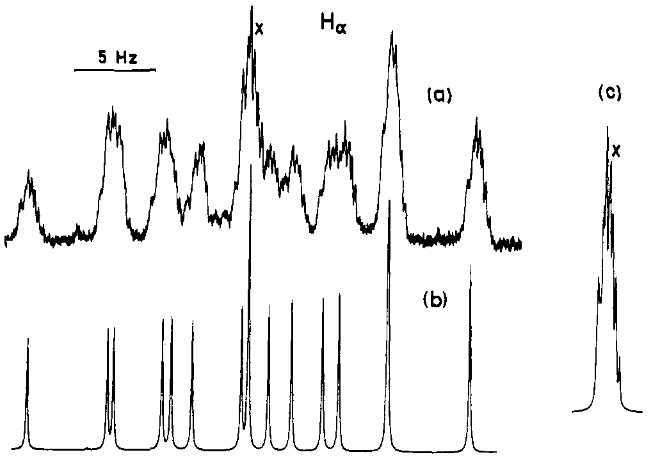
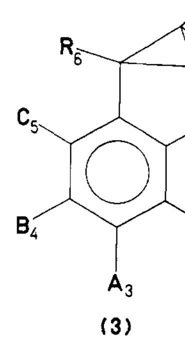


Figure 2. The observed α proton resonance of phenylcyclopropane is given in a. In b the calculated appearance of the spectrum in the absence of coupling to the phenyl protons is shown. In c the calculated multiplet for zero net magnetic moment of the β protons is displayed and can be compared with the region marked X in a. Note that this region contains overlapped multiplets (compare b) so that the comparison indicates a reliable analysis of the phenyl proton region.

Table I. Chemical Shifts and Proton Coupling Constants for Phenylcyclopropane[a] in CS_2 Solution

ν_1[b]	690.48	$^3J_{12}$	7.78	$^4J_{13}$	1.24
ν_2	707.77	$^3J_{23}$	7.43	$^4J_{15}$	2.01
ν_3	697.39	$^3J_{67}$	8.60	$^4J_{24}$	1.43
ν_6	180.0	$^3J_{69}$	5.03	$^4J_{14}$	0.56
ν_7	84.98	$^3J_{78}$	9.38	$^4J_{16}$	−0.47
ν_9	60.28	$^3J_{79}$	6.27	$^5J_{26}$	0.29
$^2J_{89}$[c,d]	−4.56	$^3J_{9,10}$	9.35	$^6J_{36}$	−0.23

[a] The numbering of shifts and couplings refers to structure **3** of the text. [b] In Hz at 100 MHz to low field of internal tetramethylsilane for a 10 mol % solution in CS_2. [c] Couplings in Hz to an estimated accuracy of 0.02 Hz. [d] The rms errors were both 0.023 Hz in the analysis of the partial spectra.



(3)

analyzed by any available computer programs (there are 1024 basis functions). However, the X and Y protons are coupled so weakly to the ring protons that any couplings manifest themselves as a slight broadening of the C protons in the ring (Figure 1). Consequently the ring proton spectrum could be analyzed as part of an ABB′ CC′R spin system, using the program LAME.[14,15] The spectrum due to the X and Y cyclopropyl protons could then be analyzed as part of an XX′YY′R spin system. The ensuing spectral parameters are given in Table I.

The observed and calculated ring proton spectra are displayed in Figure 1. Unfortunately the spectrum of proton R could not be simulated. However, Figure 2b displays the simulated spectrum for R in the absence of couplings to the ring protons. Comparison with the observed spectrum in Figure 2a indicates the correct number of peaks arising from coupling to the other cyclopropyl protons. Furthermore, one of the multiplets in the observed spectrum corresponds to spin functions of the X and Y protons describing states with a net zero magnetic moment. Hence a simulation of this multiplet is possible and is shown in Figure 2c. Allowing for overlap with other multiplets, it can be seen that the tabulated couplings between R and the ring protons satisfactorily reproduce the intensity distribution within that multiplet.

The Barrier to Internal Rotation. There is little doubt[16] that the coupling, $^6J_p{}^{H,CH}$, over six bonds between a sidechain proton and a para ring proton in toluene obeys a $\sin^2\theta$ relationship, θ being the angle by which the C-H bond of the methyl twists out of the plane of the aromatic ring. For free rotation about the C-C bond, $\langle\sin^2\theta\rangle$ is 0.5 and the observed value for $^6J_p{}^{H,CH}$ of −0.62 Hz implies that, when $\theta = 90°$, $^6J_{90}$ is −1.24 Hz if $^6J_0$ is small enough to be ignored.

INDO MO FPT calculations on ^6J in toluene are in quantitative agreement with these remarks.[16] Furthermore, the introduction of one or two methyl groups to produce ethyl[17] or isopropyl benzene introduces a predominantly twofold barrier whose magnitude can be deduced from the observed $^6J^{H,CH}$ and from a hindered rotor treatment[18,19] which yields the expectation value of $\sin^2\theta$ as a function of the barrier, of the temperature, and of the reduced moment of inertia. The presence of the methyl groups does not apparently reduce $^6J_{90}$ significantly.

Similar arguments have led to a reasonable estimate of the barrier to internal rotation in styrene,[20] where the INDO MO FPT calculations suggest a $^6J_{90}$ of −1.00 to −1.06 Hz. The smaller magnitude compared to toluene is understandable on the basis of the larger C_{ring}- - -C_α- - -H angle in styrene, the overlap with the π orbitals of the ring being reduced from the corresponding situation in toluene.

For the geometry given by the electron diffraction results,[8] our INDO MO FPT calculations yield $^6J_{90}$ as −1.11 Hz for phenylcyclopropane, falling between styrene and toluene. $^6J_p{}^{H,CH}$ in phenylcyclopropane is -0.23 ± 0.02 Hz. Hence $\langle\sin^2\theta\rangle$ is 0.21 ± 0.02. If an error of 0.1 Hz in $^6J_{90}$ is allowed, then a reduced moment of inertia of 0.37×10^{-38} g cm^2 leads[18] to a twofold barrier of 2.0 ± 0.3 kcal/mol.

Note that **1** and not **2** must be the stable conformation in this approach. If **2** were more stable than **1**, $\langle \sin^2 \theta \rangle$ would be greater than 0.5 and $^6J_p{}^{H,CH}$ would be greater than about 0.6 Hz in magnitude.

Comparison with Other Barrier Estimates. The assumption of a predominantly twofold barrier in phenylcyclopropane appears reasonable on the basis of the behavior of related molecules. For example, the corresponding twofold component of the barrier in the less symmetrical molecule, C_3H_5CHO, is 4.4 kcal/mol, while the onefold and threefold components[4] are −0.23 and 0.28 kcal/mol, respectively, less than 10% of the twofold term.

The energy difference of 1.4 kcal/mol between **1** and **2**, estimated from chemical shifts,[6] is apparently outside the experimental error of the present result. Yet no estimate of error is available for the former. However, the two measurements agree in assigning **1** to the stable conformation.

The present INDO results give **1** as more stable than **2** by 1.96 kcal/mol, the calculated dipole moments being 0.38 and 0.17 D, respectively. The measured dipole moment in benzene solution at 298 K is 0.48 ± 0.04 D, so that the semiempirical calculations indicate **1** as more stable than **2**. The calculated energy difference happens to agree exactly with the present result.

It is interesting to note that INDO calculations on toluene[16] reproduce the small barrier of 0.014 kcal/mol in toluene. Such agreements with experiment vanish in the presence of polar bonds in the molecule.[21]

The STO-3G calculations gave an energy difference of 4.3 kcal/mol between **1** and **2**. Rather expensive geometry optimization procedures would very likely reduce this number. Thus, in ethylbenzene partial geometry optimization[22] reduced the energy difference between **4** and **5** from 4.7 to 2.2 kcal/mol, whereas a thermodynamic estimate[23] gave 1.3 kcal/mol and the procedure described in this paper suggested 1.2 kcal/mol.[17]

The barrier of 5.8 kcal/mol derived from the first overtone of the torsional frequency[7] in the Raman spectrum of the liquid appears rather high. It may be noted that the same work quotes a barrier of 8.85 kcal/mol for biphenyl, whereas the proton spectrum of 4,4′-dichlorobiphenyl dissolved in a nematic liquid[24] indicates a barrier of 2 to 3 kcal/mol.

The Ring Proton Chemical Shifts. Relative to the chemical shift of 7.21 ppm for the protons of benzene dissolved in CS_2 the ortho, meta, and para protons in phenylcyclopropane are shifted to high field by 0.31, 0.13, and 0.24 ppm, respectively. The respective high-field shifts caused by a methyl group are 0.18, 0.13, and 0.17 ppm.[25] The larger shift of the ortho protons caused by the cyclopropyl group can be attributed to the magnetic anisotropy of this group. Allowing for small dilution and solvent effects on the para proton shift, its value in phenylcyclopropane is consistent with the indications, based on the dipole moment[9] and on the infrared intensity data,[10] that the cyclopropyl group is an electron donor to the phenyl π electron system.

Acknowledgments. We are grateful to the National Research Council of Canada for financial assistance.

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