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Cyclopropanes: Calculation of NMR Spectra by Ab Initio Methodology

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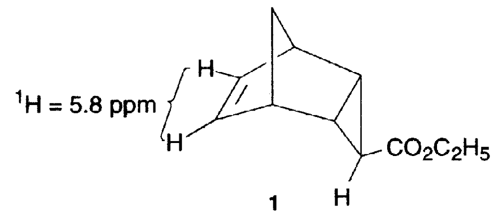
Abstract: ^1H and ^{13}C nuclear magnetic resonance chemical shifts for a select group of cyclopropyl systems were calculated using ab initio/gauge-independent atomic orbital methodology. Long range nucleus independent chemical shifts attributable to cyclopropane ring currents were estimated. The results demonstrate the viability of this protocol to simulate unusual long range shielding/deshielding effects associated with cyclopropyl systems. Examination of the molecular orbitals of bicyclo[3.1.0]-hexyl systems revealed a highly delocalized HOMO for the *anti*-conformer (pseudo-chair form). Natural atomic population analyses were used to examine putative correlations between atomic charges and chemical shifts.

Cyclopropane and its derivatives have fascinated chemists for centuries for their unique reactivity as well as unusual spectroscopic properties.[1] An early clue as to their electronic structure was provided by Lacher, Pollack and Park in 1952 who observed an unusually large magnetic susceptibility for cyclopropane and proposed a ring current model to rationalize this finding.[2] Wiberg and Nist in 1961 acknowledged that the upfield ^1H nmr shift of cyclopropyl protons could be a consequence of this property.[3] The first examples of long range ^1H shielding attributed to cyclopropane ring currents appeared in 1963[4,5] and the configurations of **1** and **2** were correctly assigned on this basis. Semi-quantitative analyses of these shifts incorporated cyclic electron delocalization models, *i.e.* ring currents, as well as methods based on empirically deduced carbon-carbon bond anisotropies.[5,6]



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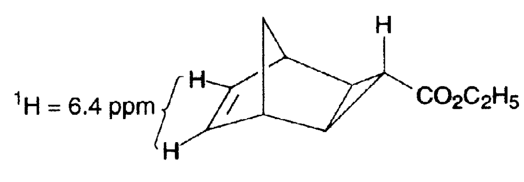

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More recently, ^{13}C nmr studies of polycyclic molecules have provided numerous examples of large upfield (-11 to -15 ppm) and downfield (+6 to +13 ppm) shifts at carbon atoms once-removed from cyclopropane rings. Typically these shifts were observed at the positions labeled ***gauche*-γ** and ***anti*-γ** in molecules with methano bridged configurations but not for the ethano-bridged analogs.[7] The upfield gauche-γ

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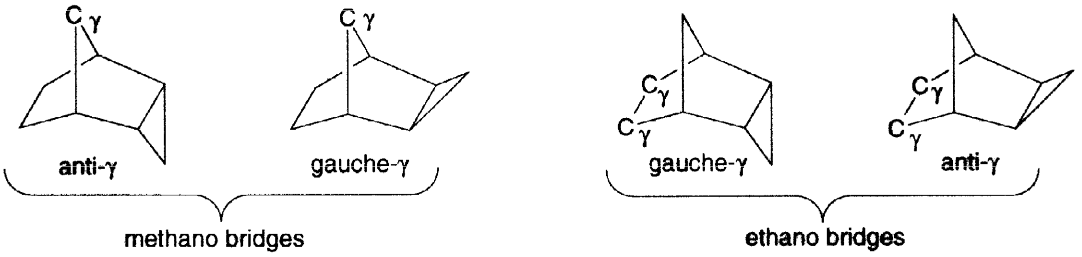


shifts have been attributed to "normal" ^{13}C steric effects by Christl[8] and Tori, *et al.*[9] Christl proposed that the downfield shifts at *anti*-γ carbons in methano-bridged systems are the result of a decrease in electron density at *anti*-γ-carbon atoms attributed to charge transfer between HOMO's of the adjacent ring bonds and unoccupied Walsh type cyclopropane orbitals (see below).[8]

The development of quantum chemical methods for computation of nuclear magnetic resonance properties[10,11,12] encouraged us to explore the use of gauge-independent atomic orbital (GAIO) methodology[11] to simulate these ^{1}H and ^{13}C chemical shifts for cyclopropyl containing systems. An obvious problem with this approach are the limitations for large molecules caused by the opposing requirements of reasonable basis sets *vs* computer time. For this reason, density functional theory (DFT) methods were used to generate geometric parameters and Hartree-Fock protocol was used for GAIO calculations. A recent review points out that in those cases where correlation is not likely to be important, the Hartree-Fock approach is adequate for the determination of chemical shielding.[10] Higher accuracy may be expected in comparisons of chemical shift differences between similar molecules due to compensation of errors.

Computational Methodology.

The Gaussian94 suite of programs was used throughout.[13] All geometries were optimized at the HF/6-31G(d) and Becke3LYP/6-31G(d)[14] level or as noted. Vibrational analyses at the HF level established the nature of the stationary points as minima (no imaginary frequencies). Absolute ^{1}H and ^{13}C isotropic shifts were determined at the RHF/6-31+G(d)//B3LYP/6-31G(d) level or as noted. Chemical shifts were determined by comparisons with the ^{1}H and ^{13}C isotropic shifts computed for tetramethylsilane at the same level. In select cases we approximated the cyclopropane ring current effects for remote atoms by replacing all carbon atoms attached to the cyclopropane rings of a given optimized structure with hydrogen atoms and excising all extraneous atoms. This procedure preserves the relative geometry between the cyclopropyl ring and the atom in question. The nucleus independent chemical shifts (NICS) of the remote atoms of interest were evaluated by replacing them with "ghost" atoms.[15]

Results.

The first stage of this study involved chemical shift calculations for cyclopropane itself to illustrate the accuracy of the methodology. The geometry and energy of cyclopropane were optimized at the B3LYP/6-311+G(d,p) level followed by three separate calculations of the GAIO magnetic shielding tensors using the following levels: RHF/6-31+G(d), RHF/6-311+G(d,p), and B3LYP/6-311+G(d,p). ^{1}H and ^{13}C chemical shifts were computed by comparisons of the magnetic shielding tensors obtained for tetramethylsilane at the same levels (**Table 1**). The agreement between calculated and experimental chemical shifts for cyclopropane is very good based on the "4 % rule" defined by Chestnut, *i.e.*, < 8 ppm for carbon resonances and < 0.34 ppm (after scaling by 0.9438) for hydrogen.[10]

Table 1: ^{1}H and ^{13}C Chemical Shift Calculations (ppm) for Cyclopropane^{a,b}

Nucleus	Basis Set	Isotropic Shielding Tensors: Tetramethylsilane	Isotropic Shielding Tensors: Cyclopropane^{a}	Calculated Chemical Shifts
^{1}H	RHF/6-31+G(d)	32.526	32.3706	0.155
^{1}H	RHF/6-311+G(d,p)	32.140	32.0563	0.084
^{1}H	B3LYP/6-311+G(d,p)	31.900	31.7903	1.11
^{13}C	RHF/6-31+G(d)	200.17	204.5103	-4.34
^{13}C	RHF/6-311+G(d,p)	194.10	198.0193	-3.92
^{13}C	B3LYP/6-311+G(d,p)	183.39	185.0094	-1.61

^{a} Geometry at B3LYP/6-311+G(d,p) level. ^{b} experimental values: ^{1}H: 0.222 ppm[16a]; ^{13}C: -3.8ppm.[12c]

As an aid in understanding long range effects it was of interest to evaluate nucleus independent chemical shifts calculated by these MO quantum methods.[15] The results evaluated using Hartree-Fock and DFT methods are shown in **Table 2** along with comparisons with induced shieldings calculated at various distances normal to the center of the molecular plane by the Johnson-Bovey model.[17] The agreement is very good, especially at distances > 2.5 Å beyond which local effects are expected to be minor.

Table 2: NICS Calculations for Cyclopropane

Distance Å	RHF/6-31+G(d)	RHF/6-311+G(d,p)	B3LYP/6-311+G(d,p)	Johnson-Bovey
0.000	-43.4129	-43.0444	-42.7322	-
0.500	-25.7859	-25.5499	-24.8455	-
1.000	-9.4322	-9.3654	-8.6586	-6.2
1.500	-4.0044	-3.9519	-3.6377	-3.0
2.000	-1.9318	-1.9097	-1.8125	-1.6
2.500	-1.0097	-0.9961	-0.9772	-0.90
3.000	-0.5731	-0.5623	-0.5644	-0.56
3.500	-0.3508	-0.3411	-0.3461	-0.36
4.000	-0.2288	-0.2202	-0.2243	-0.25

Lastly, the anisotropy of magnetic susceptibility at the B3LYP/6-311+G(d,p) level was evaluated using the individual gauges for atoms in molecules (IGIAM) method of Keith and Bader.[18] Delocalization was signaled by the finding of a significant negative anisotropy: -10.01(ppm cgs), about 1/3 the value for cyclopropenium ion. Jiao, *et al.* recently reported a small exaltation of magnetic susceptibility for cyclopropane: -4.2 ppm cgs *vs*. -14.5 ppm cgs for benzene.[19]

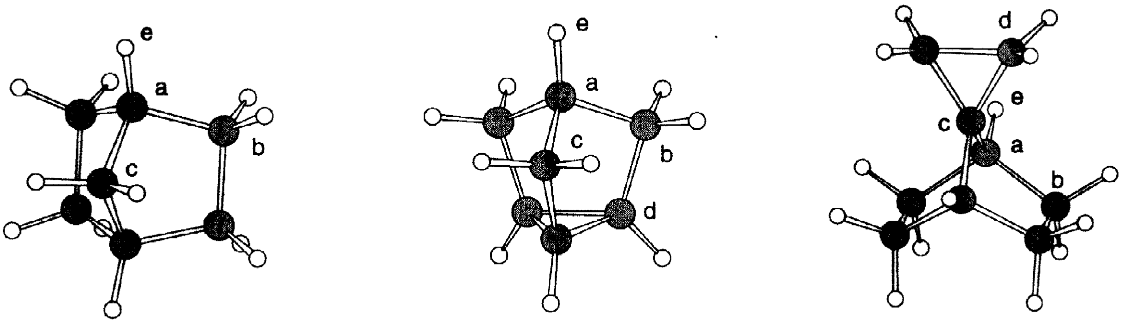
In the sequel, ^{1}H and ^{13}C chemical shift data for cyclopropane containing systems were calculated at the RHF/6-31+G(d)//B3LYP/6-31G(d) level and presented in the Tables. In general, this methodology proved to be useful for simulation of both the unusual upfield and downfield γ-shifts mentioned above, *i.e.*, calculated

^{13}C chemical shifts were within *ca.* 3-6 ppm of experimental values and ^{1}H shifts fell within 0.3-0.5 ppm of experimental values.

The calculated spectral data for norbornane and nortricyclene (**Figure 1**) fall within the guidelines mentioned above (**Table 3**). The brigdehead proton **e** of nortricyclene experiences an upfield shift (-0.29 ppm) relative to the bridgehead proton in norbornane that can be attributed to ring current effects from the cyclopropyl ring. The calculated NICS value for an atom at the same distance from the cyclopropane plane is -0.46 ppm.

Table 3: ^{13}C, ^{1}H Chemical Shift Calculations on Norbornanes and Nortricyclene (ppm)

System:	3		4		5	
Carbon/ Hydrogen	calc.	lit.[20]	calc.	lit.[21]	calc.	lit.[22]
a	33.2	38.1/37.3	27.2	29.9	38.0	41.4
b	27.4	31.5/30.6	30.2	33.4	27.4	29.4
c	34.4	40.2/39.2	30.2	33.4	26.4	32.5
d	-	-	7.1	10.3	4.3	4.9
e	1.91	2.20	1.66	1.91	1.16	na



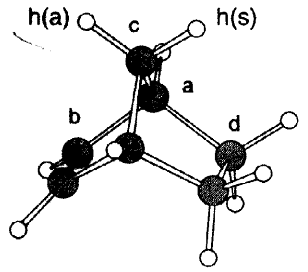
norbornane: **3** nortricyclene: **4** 7,7-spirocyclopropylnorbornane: **5**

Figure 1

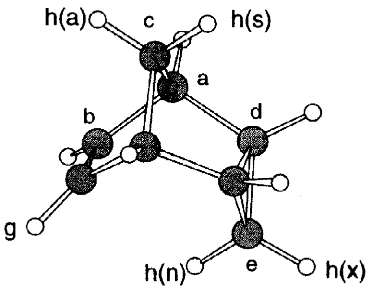
The relative shielding calculated for the bridgehead carbon **a** (-6.0 ppm) in nortricyclene *vs* norbornane is in good agreement with the experimental range (-8.2 to -6.7 ppm). The magnitude of the ^{13}C shielding is considerably larger than that expected from a NICS calculation (1.6 ppm) for a nucleus located directly above the center of the cyclopropane ring at the same distance. The enhanced shielding of the bridgehead carbon is the combined result of anisotropic effects of other bonds, hybridization differences, and to a lesser extent, delocalization effects associated with the cyclopropyl ring (see below).[6b]

Ring current effects of the cyclopropyl ring in 7,7-spirocyclopropylnorbornane are expected to be felt at the bridgehead protons. The upfield shift (-0.75 ppm) calculated by NICS methods for the bridgehead hydrogen atoms leads to a predicted chemical shift of 1.45 ppm (2.20-0.75). Ring current effects on the methylene protons are expected to be small and positive (<< 0.1 ppm) since these atoms lie nearly in the plane of the cyclopropyl ring. Unfortunately, it was not possible to obtain experimental verification of these expectations due to poor spectral resolution in the proton spectrum of spiro system. The reported range of chemical shifts of non-cyclopropyl protons was 1.1-1.9 ppm. The 4.8 ppm shielding calculated for carbon **a** in the spiro compound relative to the corresponding carbon in norbornane is in good agreement with experimental values (3.3 - 4.1 ppm). No "cyclopropyl" effect on the chemical shifts of the four ring carbons (**b**) was found in agreement with experiment (1.2 - 2.1 ppm).

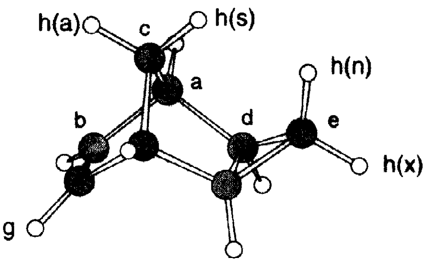
In the present context, it was of interest to examine the ^{1}H and ^{13}C chemical shifts of the hydrocarbon systems corresponding to tricyclo[3.2.1.0^{2,4}]octenes **1** and **2.** Major challenges in these systems were to reproduce the ~0.6-0.7 ppm downfield chemical shift of the olefinic protons in the *endo*-isomers and the 25.7 ppm difference in chemical shift between the bridge carbons **c** for the parent systems **7** and **8.** Both of these objectives were met. The calculated shift for the olefinic protons was 0.71 ppm and the cyclopropyl ring current contribution was estimated to be *ca.* 0.35 ppm by a NICS calculation. Calculated ^{13}C chemical shifts for the alkene carbons were in satisfactory agreement with literature values (**Table 4**) including the 10 ppm downfield shift in the *endo*-isomer relative to the *exo*-isomer. Of especial significance, the shifts of the bridge carbons **c** relative to norbornene were accurately reproduced (found, calculated) : *exo vs.* norbornene (-11.1 ppm, -9.1 ppm); *endo vs* norbornene (15.2, 14.3 ppm).



norbornene: **6**



endo-tricyclo[3.2.1.0^{2,4}]-
norbornene: **7**

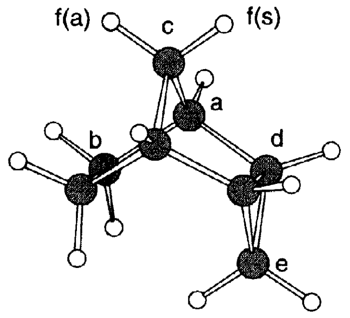


exo-tricyclo[3.2.1.0^{2,4}]-
norbornene: **8**

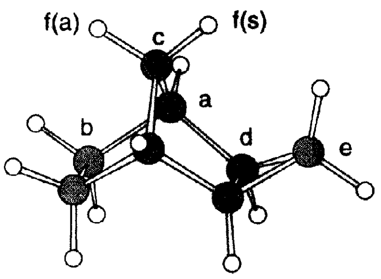
Table 4: ^{13}C, ^{1}H Chemical Shift Calculations on Norbornenes (ppm)

System:	6		7		8	
Carbon/ Hydrogen	calc.	lit.[9]	calc.	lit.[9]	calc.	lit.[9]
a	36.9	41.8	38.2	42.3	37.5	41.4
b	136.4	135.2	132.5	130.4	142.3	141.1
c	45.5	48.5	59.8	63.7	36.4	37.4
d	24.3	24.6	9.0	12.3	18.3	21.9
e	-	-	14.9	17.1	17.6	19.2
g	6.45	5.93	6.14	5.64	6.85	6.32
h(s) h(a)	1.06(s) 1.34(a)	1.07(s) 1.32(a)	1.75(s) 1.58(a)	1.67(a) 1.76(s)	0.90(s) 0.87(a)	1.11(s) 0.84(a)
h(x) h(n)	- -	- -	0.49(x) 0.36(n)	0.54(x) 0.34(n)	0.72(x) 1.35(n)	0.75(x) 1.43(n)

The related properties of the saturated analogs **9** and **10** were similarly well reproduced (**Table 5**), including the remarkable 26.7-26.9 ppm shielding difference between the bridge carbons **c** (calculated: 23.3 ppm). The small upfield shift for the ethano-bridge carbons **b** of *endo*-tricyclo[3.2.1.0^{2,4}]norbornane (**9**) relative to those in norbornane is 2.5 ppm in good agreement with experimental values (3.8-4.3 ppm). The large (1.1 ppm) predicted shift difference for the bridge protons f(s) and f(a) could not be validated experimentally. However, the chemical shifts of the H-C-O protons of the epimeric *anti*-8-hydroxy analogs **12** and **13** serve as useful models for the *syn*-protons f(s).[4] In these systems Δδ is =0.67 ppm, in reasonable agreement with the calculated difference for the unsubstituted analogs (Δδ =1.1 ppm).



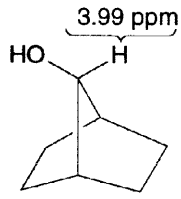
endo-tricyclo[3.2.1.0^{2,4}]norbornane: **9**



exo-tricyclo[3.2.1.0^{2,4}]norbornane: **10**

Table 5: ^{13}C, ^{1}H Chemical Shift Calculations on Tricyclonorbornanes (ppm)

System:	3		9		10	
Carbon/ Hydrogen	calc.	lit.[20]	calc.	lit.[20b,23]	calc.	lit.[20b,23]
a	33.2	38.1/37.3	33.2	36.6/37.2	32.2	35.7/35.9
b	27.4	31.5/30.6	24.9	26.8/27.2	27.9	29.8/30.0
c	34.4	40.2/39.2	48.3	53.5/53.8	25.0	26.8/26.9
d	-	-	17.6	23.1/23.5	10.2	14.7/14.8
e	-	-	15.1	17.7/17.9	2.2	1.0/1.2
f(s)	1.13	1.21	1.81	na	0.74	na
f(a)	1.13	1.21	1.26	na	0.57	na



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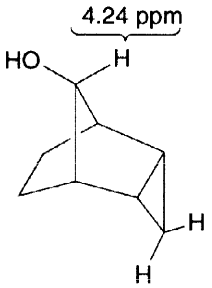

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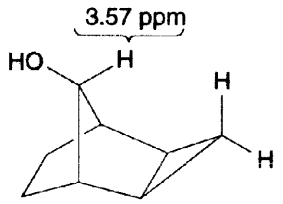
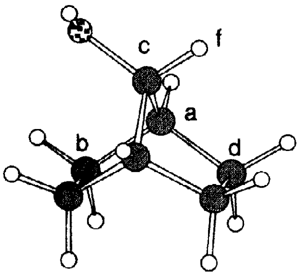


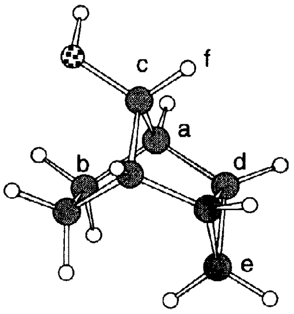
13

In contrast to the properties of the *exo*-tricyclic hydrocarbons in Tables 4 and 5, bridge carbon **c** resonance of **13** was reported to be 7.1 ppm *downfield* from the bridge carbon in 7-norbornanol.[20b] In view of this puzzling discrepancy we extended this study to include the alcohols **11**, **12** and **13** The calculated results for these three alcohols (**Table 6**) are entirely consistent with those of the hydrocarbons in that the calculated ^{13}C shifts of the bridge carbons are in the same relative order with δ-values increasing in the following series:

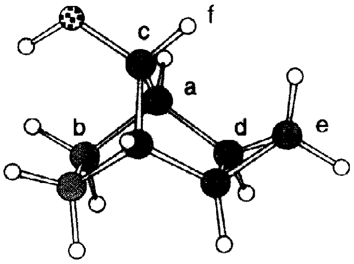
13 < **11** < **12**. In view of this and the fact that the calculated chemical shifts for carbinol protons are also in the expected relative order it is not unlikely that the configuration of this compound has been incorrectly assigned.[24]



7-norbornanol: **11**



endo-tricyclo-7-norbornanol: **12**

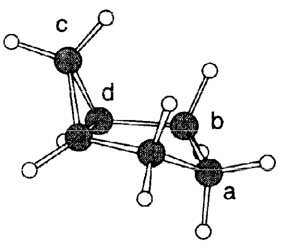


exo-tricyclo-7-norbornanol: **13**

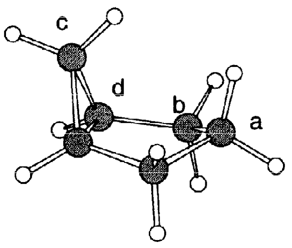
Table 6: ^{13}C,^{1}H Chemical Shift Calculations on Tricyclonorbornanols (ppm)

System:	11		12		13	
Carbon/ Hydrogen	calc.	lit.[20b,25]	calc.	lit.[4,20b]	calc.	lit.[4,20b]
a	36.6	40.4	37.7	40.0 ?	35.4	40.0 ?
b	25.0	26.5	22.7	24.0 ?	24.8	24.0 ?
c	71.6	79.5	79.5	86.6 ?	64.7	86.6 ?
d	24.8	27.0	11.3	15.6 ?	10.3	15.6 ?
e	-	-	9.3	17.3 ?	2.3	17.3 ?
f	3.61	3.99	3.81	4.24	3.18	3.57

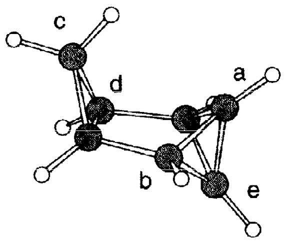
We next addressed the question of whether the chemical shift changes could be related to differences in charge density induced by interactions between cyclopropane orbitals and remote ring bonds as suggested by Christl.[8] For this purpose we examined the properties of the chair and boat forms of bicyclo[3.1.0]hexane and tetracyclo[4.1.0.0^{2,4}0^{3,5}]heptane. The former structures incorporate the essential features of the more complex analogs and are amenable to computation at higher levels of theory than is feasible with the larger molecules. The latter system offers the opportunity to make an internal comparison of boat and chair carbons. An additional challenge was to verify that the structure of the preferred conformer of bicyclo[3.1.0]hexane determined by microwave spectroscopy is the boat form. This second objective was fulfilled by calculations at the MP2/6-31G(d) level which gave rise to a 3.45 kcal/mol difference in energy in favor of the boat conformer and 3.00 kcal/mol at the B3LYP/6-31G(d) level (both values corrected for zero point energy differences at HF/6-31G*).



bicyclo[3.1.0]hexane: chair: **15**



bicyclo[3.1.0]hexane: boat: **16**



tetracyclo[4.1.0.0^{2,4}0^{3,5}]heptane: **17**

The computed nmr parameters and geometry for the boat conformer were fully consistent with the experimental values (**Table 7**).[26] The calculated ^{13}C chemical shifts for the *gauche* and *anti*-γ carbons of the conformers **15** and **16** are ordered in the same relative sense as those in the more complex examples discussed earlier in that they bracket the ^{13}C shift for the reference molecule cyclohexane. Likewise, the calculated chemical shifts for the related carbons in **17** are consistent with expectations and experiment. Christl suggested that the underlying reason for the downfield shift for *anti*-γ carbons of chair forms was caused by decreased electron density at that position (carbon 3) brought about by interaction of the LUMO of the cyclopropane ring with the filled orbitals of the sigma system of the C-C-C framework (structure A in **Figure 2**).[8] It was reasoned that because the alignment of these orbitals in the chair form is more favorable than in the boat form a decrease in the electron density at C3 in the former would cause deshielding at this center. This conclusion was supported by calculations of charge densities using MINDO/2 and ab initio STO-3G methods.

Table 7: $^{13}C,^{1}H$ Chemical Shift Calculations on Cyclohexane, 15, 16, 17 (ppm)

System	Cyclohexane		**15**	**16**		**17**	
Carbon	calc.	lit.[27,16b]	calc.	calc.	lit.[8]	calc.	lit.[8]
a	24.7	27.8	32.8	20.1	20.2	-6.11	-4.0
b	-	-	28.9	25.9	27.6	31.24	38.4
c	-	-	19.8	5.2	5.8	15.15	17.6
d	-	-	16.7	12.9	16.7	13.83	17.3
e	-	-	-	-	-	17.06	22.1

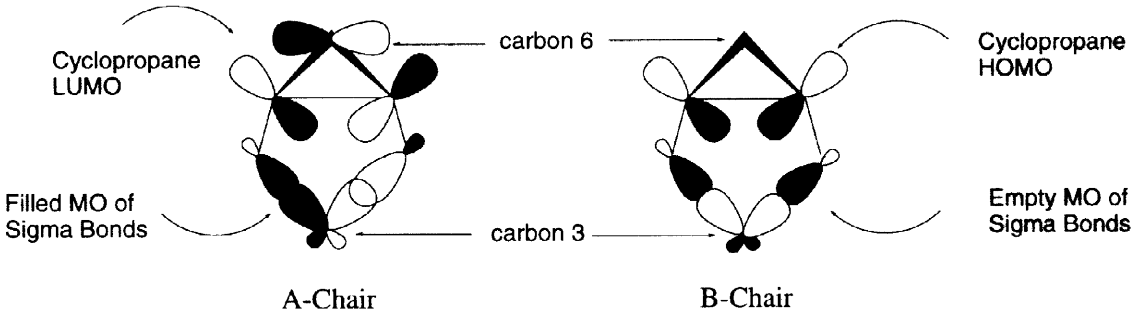


Figure 2

Consistent with this proposal, the atomic charges calculated at carbon 3 by a natural population analysis (NPA)[28] showed a reduced charge for **15** (-0.372) relative to both cyclohexane **14** (-0.379) and the boat form **16** (-0.388) at the B3LYP/6-311+G*//MP2/6-31G* level.[29] Although these results suffice to rationalize the greater deshielding at carbon 3 in the chair form relative to cyclohexane, the magnitude of the calculated charge differences (0.007) is on the edge of reliability. A corollary to the above analysis requires that the sum of the charges of the atoms of the cyclopropyl group be more negative in the chair form than in the boat form. Our results lead to the opposite finding for both the cyclopropyl carbon framework alone: -0.849 (boat) *vs* -0.837 (chair) or for the sum of the charges of the cyclopropyl carbons plus the attached hydrogen atoms: -0.0274 (boat) *vs* -0.0218 (chair). It is clear that other MO's effect the overall charge distribution (see below).

Nevertheless, we extended these comparisons to more complex systems to test the generality of the above correlations. **Table 8** lists npa calculated atomic charges and the ^{13}C chemical shifts for "γ" carbon atoms for the systems discussed earlier at the B3LYP/6-31G* level. These charges are compared with chemical shifts relative to the appropriate carbon in reference compounds. Although these data are consistent with the HOMO-LUMO analysis of Christl, the calculated charge differences in at least two of these examples are unreliably small .

Table 8: Comparison of NPA Charges with Chemical Shifts: Chair vs Reference

Systems	Chair Forms		Reference System		Δ Charge	Δ δ ppm Calculated	Δ δ ppm Experimental
	charge	δ	charge	δ	chair-ref	chair-ref	chair-ref
15 - 14	-.451	32.8	-.460	24.7	0.009	8.1	na
7 - 6	-.422	59.8	-.441	45.5	0.019	14.3	15.2
9 - 3	-.448	48.3	-.465	34.4	0.017	13.9	13.3-14.6
12 - 11	+.106	79.5	+.0947	71.6	0.011	7.9	na

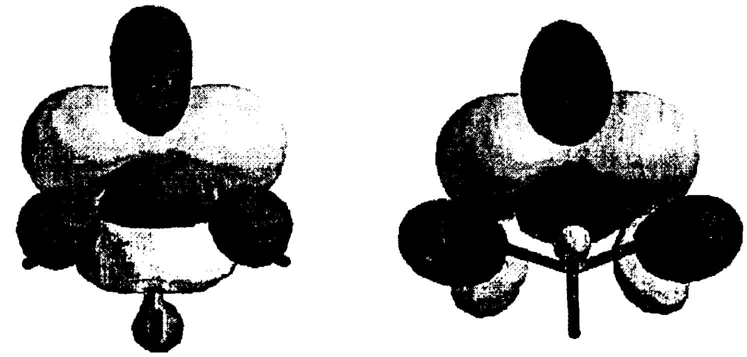
In **Table 9** we compare charge differences between "γ" carbon atoms in chair *vs* boat forms with chemical shifts. Although the same general trends are observed the correlation is more problematic, possibly as a consequence of steric deshielding caused by close interatomic contacts in some of the boat forms.[30]

Table 9: Comparison of NPA Charges with Chemical Shifts: Chair vs Boat Forms

Systems	Boat Forms		Chair Forms		Δ Charge	Δ δ ppm	Δ δ ppm
	charge	δ	charge	δ	chair-boat	chair-boat Calculated	chair-boat Experimental
15 -16	-.468	20.2	-.451	32.8	0.017	12.6	na
7 - 8	-.446	36.4	-.422	59.8	0.024	23.4	26.3
9 - 10	-.468	25.0	-.448	48.3	0.020	23.3	26.7-26.9
12 -13	.0986	64.7	.106	79.5	0.0074	14.8	na
17	-.256	-6.1	-.232	17.1	0.024	23.2	26.1

In view of the above it was of interest to examine the properties of the HOMO and HOMO-1 molecular orbitals for the chair and boat forms of bicyclo[3.1.0]hexane to get a more realistic view of the importance of delocalization of sigma orbitals of the framework. Electron density plots[31] of these orbitals shown below (**Figure 3**) demonstrate that the HOMO of the chair form is in fact more highly delocalized than that of the boat form in support of Christl's qualitative MO analysis. The symmetry of highest occupied molecular orbitals of both the chair and boat forms is $_1$A', however. In the chair form, this array can be visualized as arising in part from interaction of a cyclopropane HOMO with a LUMO of the sigma bonds (**Figure 2**, B-chair) and is expected to lead to *increased* electron density at C3. In contrast, the HOMO of the boat form places very little electron density on carbon 6. This situation is reversed on comparison of the HOMO-1 orbitals which have the $_1$A" symmetry expected for the A-chair interactions shown in **Figure 2**. Ultimately, the electron density at a given nucleus is determined by sum of the densities of all of the occupied orbitals and conclusions based on expectations for a single orbital are likely to be misleading at best.[32]

HOMO **bicyclo[3.1.0]hexane Chair** **bicyclo[3.1.0]hexane Boat**



HOMO-1 **bicyclo[3.1.0]hexane Chair** **bicyclo[3.1.0]hexane Boat**

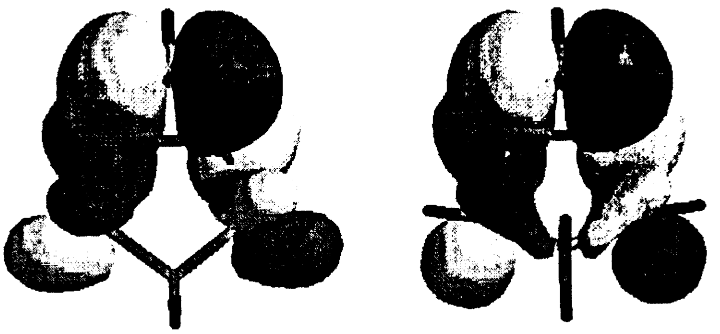


Figure 3. HOMO and HOMO-1 for Bicyclo[3.1.0]hexanes

These results highlight some of the complexities involved in predicting chemical shifts for cyclopropane containing molecules.[33] Fortunately, their more outstanding nmr characteristics can be reproduced reliably using GIAO/SCF methodology and relatively small basis sets. Ring current effects attributable to induced magnetic fields in cyclopropane play a minor role in ^{13}C spectra, but can induce significant shieldings in proton spectra. Correlations of chemical shifts with calculated charge density are not expected to be generally useful in view of the small differences found and the arbitrary nature of assigning charge in quantum calculations.

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29. The results at the MP2/6-31G* level were similar: **15** (-0.453); **14** (-0.463); **16** (-0.472).

30. For example, the interatomic separations between the proximate protons on carbons **c** and **e** in compounds **8** and **10** are 1.984 Å and 2.036 Å , respectively.

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33. Table 10 lists total energies and zero-point energies for most of the molecules in the text.

Table 10: Total Energies (hartrees) and Zero-Point Energies (hartrees/particle)

	HF/6-31G(d)		B3LYP/6-31G(d)
Compound	Energy	ZPE	Energy
3	-272.0612001	0.190008	-273.9684864
4	-270.8677138	0.165082	-272.7317913
5	-348.927764	0.226039	-351.3507324
6	-270.8618412	0.164572	-272.7274223
7	-308.6791815	0.170468	-310.7843862
8	-308.6832126	0.170770	-310.7875400
9	-309.8796957	0.196404	-312.0259851
10	-309.8891676	0.196499	-312.0343870
11	-346.9125833	0.195237	-349.1772291
12	-384.7330246	0.201566	-387.2366365
13	-384.7256529	0.199168	-387.2405217
15	-232.9956295	0.157060	-234.6257157
16	-233.0010647	0.157379	-234.6308212
17	-269.6036203	0.137630	-271.4308152