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Ab Initio IGLO MO Studies of the Conformational (Pucker Angle) and Substituent Dependencies of Isotropic ^{13}C Chemical Shifts in 1-Substituted Cyclobutanes and Bicyclo[1.1.1]pentanes

Michael Barfield

Contribution from the Department of Chemistry, University of Arizona, Tucson, Arizona 85721

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Abstract: Ab initio IGLO (individual gauge for localized molecular orbital) methods of SCF-MO theory are used to study and analyze the mathematical form of the conformational dependencies of the isotropic ^{13}C chemical shifts of cyclobutane and nitrile, methyl, and fluoro derivatives. Also included in this study are bicyclo[1.1.1]pentanes with the same substituents as these provide an upper limit for the pucker angle in four-membered rings. Calculated ^{13}C chemical shifts for all molecules in their energy optimized (HF/6-31G** level) equilibrium geometries compare favorably with the experimental data. Pucker angle averaging is a relatively small effect in which chemical shifts differ from the equilibrium geometry values by 1.0 ppm at most. Predictions that the effects of increasing strain will be to shift all the ring carbons to higher frequency except for the C1 carbon of 1-fluoro- compounds are confirmed by the experimental shifts for the 1-substituted bicyclo[1.1.1]pentanes. Conformational and substituent effects are analyzed in terms of the angular dependence of the IGLO C–H and C–C bond paramagnetic contributions, and these are especially important for equatorial C–H or C–X bonds. Also examined are the angular dependencies of α-, β-, and γ-effects for the ring carbons for the three substituents. The prediction that these will be more shielding for dihedral angles in the range of about 110–160° is qualitatively in conformity with experimental data in the bicyclo[*n*.1.1]alkanes series.

I. Introduction

Ab initio molecular orbital methods have been used to investigate the conformational dependencies of ^{13}C chemical shifts in the NMR spectra of aliphatic and alicyclic hydrocarbons.[1-3] Calculated results for the orientational dependence of γ-substituent effects[4] in model compounds are in reasonably good agreement with experimental data for rigid bicyclic molecules.[2] On the basis of these studies it is now clear that α- and β-effects are also strongly dependent on conformation.[1,2] The sensitivity of ^{13}C NMR chemical shifts to conformational features offers promise for estimating dihedral angles in cyclic molecules.[2] Not included in these studies[1-3,5] of ^{13}C chemical shielding was the importance of internal angle changes such as occur in small strained molecules. For example, the ^{13}C NMR studies of unusual polymers, which have all 1,3-fused cyclobutane rings in the backbone,[6,7] show the chemical shifts depend on the ring pucker angles. Although the importance of the pucker angle dependence of ^{13}C chemical shifts is not widely recognized in four-membered rings, recently these have been shown to provide a useful criterion for ring puckering in five-membered rings.[8-10]

Carbon-13 NMR studies of cyclobutane[11,12] and substituted cyclobutanes[13-16] include those from this laboratory.[6,7] The ^{13}C shielding tensor data from low-temperature NMR data[17] for a number of cyclic molecules including cyclobutane and bicyclo[1.1.1]pentane have been examined with good success via the ab initio IGLO method. Cyclobutanes have also been studied from the standpoint of ring-strain and ring-puckering effects, structure, and molecular spectroscopy.[18-23] Because of the unique structural features of bicycloalkanes and the 1-substituted derivatives, their NMR parameters have been studied extensively.[24-28] Of particular interest in this study is the pucker angle dependencies of

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the ^{13}C chemical shifts in the series of bicyclo[*n*.1.1]alkanes (*n* = 1, 2, 3) because these reflect a large range of pucker angles in the highly strained four-membered rings.

A description of the computational methods for molecular structures and chemical shielding is presented in the following section. In Section III the calculated ^{13}C chemical shifts for all of these molecules in their equilibrium geometries are compared with the experimental data. For cyclobutane and the substituted cyclobutanes the chemical shifts are averaged over the puckering potentials. This procedure requires the angularly dependent (pucker angle) chemical shifts and energies which are described in Section IV. The conformational dependencies of the α-, β-, and γ-substituent effects, which are presented for the substituted cyclobutanes in Section V.A, provide an excellent criterion for interpreting ^{13}C chemical shift data in 1-substituted bicyclo[*n*.1.1]-alkanes in Section V.B.

II. Computational Details

A. Molecular Structures. All geometries are optimized ones, using GAMESS,[29] Gaussian 88,[30] or Gaussian 90[31] codes with split valence basis sets and polarization functions at the HF/6-31G** levels.[32] Initially, smaller basis sets were used for geometry optimization, but the shielding results, especially for cyclobutanecarbonitrile and fluorocyclobutane, were found to be extremely basis set dependent. The sensitivity of chemical shielding to geometrical factors is consistent with observations of others,[3,33] and it is now clear that energy optimized geometries for shielding calculations require good quality basis sets. Bond lengths and bond angles for the energy optimized structures for cyclobutane (**1**), and equatorial and axial arrangements of cyclobutanecarbonitrile (**2e** and **2a**), methylcyclobutane (**3e** and **3a**), and fluorocyclobutane (**4e** and **4a**) are depicted in Figure 1. Energy optimized structures for cyclobutane have been reported previously with basis sets of comparable quality.[19-22] These geometries are in reasonable agreement with structural data[34] from NMR,[35] rotational spectroscopy,[36] infrared, and electron diffraction[37] studies. The major improvement in the structure of cyclobutane (and bicyclo[1.1.1]pentane) optimized at the MP2/6-31G* level appears to be C–H bond lengths which are longer by about 0.01 Å.[22c]

Previously reported geometries for axial and equatorial cyclobutanecarbonitrile[38] were based on somewhat smaller basis sets, but the results are comparable to those in Figure 1. Both sets of calculations are in reasonable agreement with the available electron diffraction data,[39] except for two of the bond lengths. The calculated C1—C5 and C5≡N bond lengths of 1.467 and 1.136 Å are respectively larger and smaller than the experimental values of 1.454 and 1.156 Å. These differences are undoubtedly related to a several ppm disparity noted here between the calculated and experimental ^{13}C chemical shifts for the CN carbon. Although there have been several spectroscopic and ab initio MO studies of methylcyclobutane (**3**)[40,20] and fluorocyclobutane (**4**),[41,42] little structural data appear to be available for comparison.

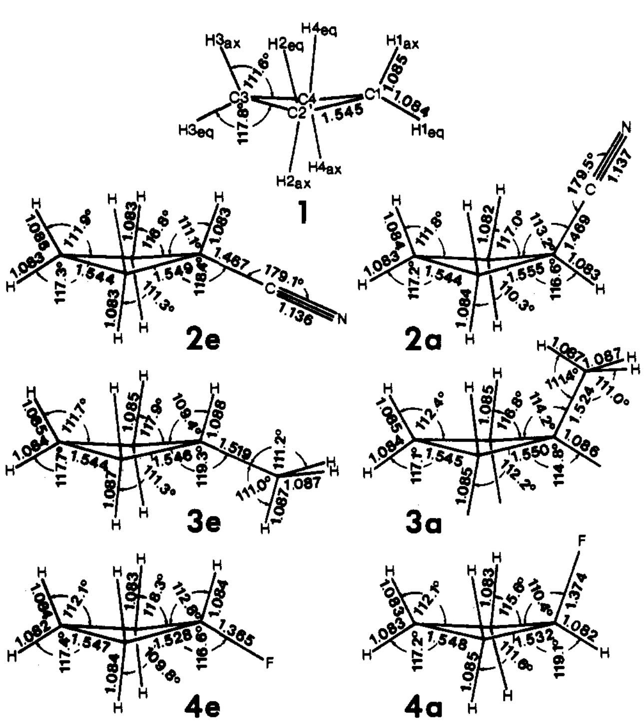

Figure 1. Energy optimized (HF/6-31G**) structures of cyclobutane (**1**) [dihedral angles: ∠H1$_{ax}$–C1–C2–C3, –94.33°; ∠H1$_{eq}$–C1–C2–C3, 139.23°], *eq*-cyclobutanecarbonitrile (**2e**) [dihedral angles: ∠N–C5–C1–C2, –52.38°; ∠N–C5–C1–H1$_{ax}$, 180.00°; ∠C5–C1–C2–C3, 140.75°; ∠C5–C1–C2–H2$_{eq}$, –98.19°; ∠C5–C1–C2–H2$_{ax}$, 27.89°; ∠C1–C2–C3–H3$_{eq}$, –139.49°; ∠C1–C2–C3–H3$_{ax}$, 93.95°], *ax*-cyclobutanecarbonitrile (**2a**) [∠N–C5–C1–C2, 49.23°; ∠N–C5–C1–H1$_{eq}$, 180.00°; ∠C5–C1–C2–C3, –98.20°; ∠C5–C1–C2–H2$_{eq}$, 22.98°; ∠C5–C1–C2–H2$_{ax}$, 148.33°; ∠C1–C2–C3–H3$_{eq}$, –136.81°; ∠C1–C2–C3–H3$_{ax}$, 96.67°], *eq*-methylcyclobutane (**3e**) [∠H5–C5–C1–H1$_{ax}$, 180.00°; ∠H5′–C5–C1–H1$_{ax}$, 60.01°; ∠C5–C1–C2–C3, 141.75°; ∠C5–C1–C2–H2$_{eq}$, –97.03°; ∠C5–C1–C2–H2$_{ax}$, 29.19°; ∠C1–C2–C3–H3$_{eq}$, –139.56°; ∠C1–C2–C3–H3$_{ax}$, 93.91°], *ax*-methylcyclobutane (**3e**) [∠H5–C5–C1–H1$_{ax}$, 180.00°; ∠H5′–C5–C1–H1$_{ax}$, 60.00°; ∠C5–C1–C2–C3, 100.43°; ∠C5–C1–C2–H2$_{eq}$, 20.03°; ∠C5–C1–C2–H2$_{ax}$, 145.96°; ∠C1–C2–C3–H3$_{eq}$, –135.63°; ∠C1–C2–C3–H3$_{ax}$, 98.22°], *eq*-fluorocyclobutane (**4e**) [∠F–C1–C2–C3, 140.11°; ∠H1$_{ax}$–C1–C2–C3, –94.38°; ∠F–C1–C2–H2$_{eq}$, –98.26°; ∠F–C1–C2–H2$_{ax}$, 28.23°; ∠C1–C2–C3–H3$_{eq}$, –140.11°; ∠C1–C2–C3–H2$_{ax}$, 93.13°], and *ax*-fluorocyclobutane (**4a**) [∠F–C1–C2–C3, –95.01°; ∠H1$_{eq}$–C1–C2–C3, 140.06°; ∠F–C1–C2–H2$_{eq}$, 25.84°; ∠F–C1–C2–H2$_{ax}$, 151.50°; ∠C1–C2–C3–H3$_{eq}$, –136.37°; ∠C1–C2–C3–H3$_{ax}$, 96.75°].

In the optimized cyclobutane structures **1**–**4** there are clear trends in the calculated bond lengths which will be shown to parallel the experimental and calculated ^{13}C chemical shift patterns. For all of the molecules in Figure 1 the axial C–H bond lengths are greater than or equal to the corresponding equatorial C–H bond lengths. Moreover, within a given pair of isomers axial C–X bonds and C–H bonds at C1 are longer than the corresponding equatorial bonds. Although the differences are small (the largest computed difference between axial and equatorial bond lengths is 0.009 Å between **4a** and **4e**), with the exception of several C–H bonds the bond lengths are greater in the axial isomers than in the equatorial isomers. By far, the largest substituent induced changes in the bond lengths occur for the C1–C2 bonds in the fluoro-substituted compounds **4e** and **4a**.

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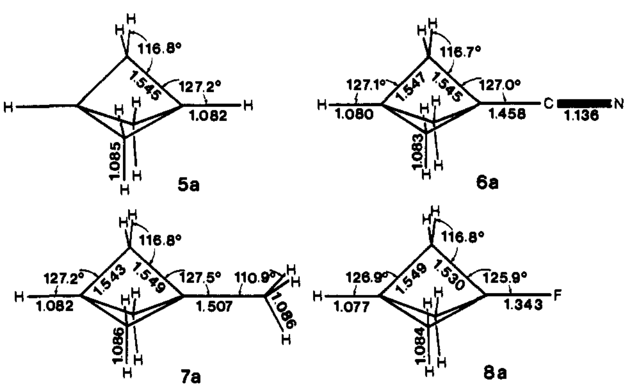

Figure 2. Energy optimized (HF/6-31G**) structures of bicyclo[1.1.1]-pentane (**5a**) [∠H1–C1–C2–H2, 67.43°], bicyclo[1.1.1]pentane-1-carbonitrile (**6a**) [∠C6–C1–C2–H2, 67.70°], 1-methylbicyclo[1.1.1]pentane (**7a**) [∠C6–C1–C2–H2, 67.35°], and 1-fluorobicyclo[1.1.1]pentane (**8a**) [∠F–C1–C2–H2, 68.07°].

Since the bicyclo[1.1.1]pentane series **5–8** corresponds to quite large pucker angles for the four-membered rings, it was of interest to compare the shielding results with those for the corresponding cyclobutanes. Depicted in Figure 2 are the energy optimized structures (HF/6-31G** level) for bicyclo[1.1.1]pentane (**5a**), bicyclo[1.1.1]pentane-1-carbonitrile (**6a**), 1-methylbicyclo[1.1.1]pentane (**7a**), and 1-fluorobicyclo[1.1.1]-pentane (**8a**). Electron diffraction data for the parent compound **5a** have been reported by Chiang and Bauer.[43] Although the calculated and experimental results for the C–C bond lengths (1.545 Å) are identical, the calculated values for the methylene H–C–H and internal C2–C1–C4 angles (111.0° and 87.2°) are substantially larger than the ones *assumed* (103.8° and 73.3°, respectively) in the electron diffraction analysis.

Further shortening of the C1–X bond lengths (and C3–H bond lengths) is noted for the four bicyclo[1.1.1]pentanes in Figure 2 compared with the equatorial C1–X bonds for the cyclobutanes in Figure 1. The largest changes of 0.005 and 0.022 Å occur for the C1–H and C1–F bond lengths in **5a** and **8a**, respectively. In this series several of the C1–C2 bonds are slightly longer than for the substituted cyclobutanes in Figure 1.

B. Shielding Calculations. All shielding calculations in this study were based on the IGLO (individual gauge for localized orbitals) formulation of Kutzelnigg et al.[3,44,45] This method has been applied with good success to a large number of calculations of shielding for elements in the first and second rows. In this method localized MO's, which are associated with inner shells, bonding orbitals, and lone pairs, have unique origins for the calculation of diamagnetic and paramagnetic terms. These methods provide a satisfactory description of chemical shielding using modest basis sets.[3,44–47] Qualitatively, this can be easily rationalized. The chemical shielding is very sensitive to the cancellation between large diamagnetic σ^d and paramagnetic contributions σ^p of opposite sign. The paramagnetic contributions are much more difficult to calculate than the diamagnetic terms, but these vanish if the origin is at the center of spherical orbitals. Since localized quantities such as bonds and lone pairs tend to be roughly spherical, the resulting decrease in paramagnetic shielding magnitudes produces smaller cancellation errors between σ^d and σ^p.

The basis sets which were used here for the shielding calculations are given in Table I. There have been extensive studies of the basis set dependence of chemical shielding,[1–3,44,45] and these are consistent with several IGLO calculations performed here at the double-ζ (DZ) level, e.g., basis set I is a (7,3/3) Huzinaga set[48] in the contraction (4111;21/21). Most of the calculations were performed with a (9,5/5) set contracted to a triple-ζ (51111/311/2111) set with one set of (5) d-type functions on elements C–F. The latter set is denoted basis set II′ in the notation of the Bochum group.[3,45] It is somewhat smaller than basis set II in using a double-ζ set on hydrogen instead of a triple-ζ set with p-type polarization functions, but the shielding results are comparable.

Table I. Basis Sets Used in the IGLO Calculations—HF/6-31G** Optimized Geometry for Methane

basis	atom	contraction	polarization function exponents	methane chemical shielding, ppm
I	C	[4111,21]		220.2
	H	[21]		
II′	C	[51111,2111]	d 1.0	201.0
	H	[21]		
II	C	[51111,2111]	d 1.0	200.6
	H	[311]	p 0.65	

Chemical shifts were obtained by subtracting the chemical shielding for the nuclei of interest from the reference compound shielding. The ^{13}C shieldings of tetramethylsilane (TMS) were not obtained with these basis sets. The methane shielding data in Table I (HF/6-31G** geometries) were computed with the three basis sets and were used with the experimental chemical shift (−2.3 ppm)[49] to provide TMS reference values. All computations were performed on Convex C220, C240 computers, or Digital Equipment Corp. workstations.

In previous studies[1,2] of conformational dependencies of chemical shifts it was noted that the ^{13}C isotropic shielding data could be represented accurately by means of Fourier series expansions of the form

$$\sigma(\varphi) = \sum_{n=1}^{9} A_n \cos n\varphi + B \tag{1}$$

where φ is the dihedral angle and the coefficients A_n and B are determined by linear regression analyses of the calculated shielding data. It is also convenient to express the energies $E(\varphi)$ as a truncated Fourier series of the same form

$$E(\varphi) = \sum_{n=1}^{6} A_n \cos n\varphi + B \tag{2}$$

with coefficients also based on linear regression analyses.

For cyclobutane and the substituted cyclobutanes the experimental ^{13}C shieldings are average values of $\sigma(\varphi)$ over the barrier $E(\varphi)$ associated with the puckering motion,

$$\langle\sigma\rangle = \int \sigma(\varphi)\, e^{-E(\varphi)/kT}\, d\varphi \Big/ \int e^{-E(\varphi)/kT}\, d\varphi \tag{3}$$

The averaged shielding data in the next section were obtained by numerical integration of eq 3.

III. Comparisons of Calculated Chemical Shifts for Cyclobutanes and Bicyclo[1.1.1]pentanes with Experimental Values

Entered in Table II are the calculated ^{13}C chemical shifts for cyclobutane (CB; **1**), cyclobutanecarbonitrile (CNCB; **2**), methylcyclobutane (MECB; **3**), fluorocyclobutane (FCB; **4**), bicyclo[1.1.1]pentane (**5a**), bicyclo[1.1.1]pentane-1-carbonitrile (**6a**), 1-methylbicyclo[1.1.1]pentane (**7a**), and 1-fluorobicyclo[1.1.1]-pentane (**8a**). Results for cyclobutane were based on IGLO basis sets I, II′, and II. As usual, calculated results improve with basis set quality and there is substantial improvement for the triple-ζ set II′ in comparison with the double-ζ set (basis set I). There is a small improvement for set II in comparison with set II′. The IGLO basis set II′ results are given for all molecules in Table II except bicyclo[1.1.1]pentane for which results are reported for basis sets I and II. Also included in Table II are the isotropic ^{13}C chemical shifts measured in chloroform-*d*. Within the cyclobutane series **1–4** the average deviation is 0.5 ppm between the calculated and experimental values for all ten carbons not including the CN carbon of CNCB and the C1 carbon of FCB.

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Table II. Calculated ^{13}C Isotropic Chemical Shifts (Basis Sets I, II, or II′) for Substituted Cyclobutanes and 1-Substituted Bicyclo[1.1.1]pentanes Compared with Experimental Values[a]

		C1	C2,C4	C3	CN/Me
		Cyclobutane (**1**)			
basis I[b]	δ	14.8	14.8	14.8	
basis II′ [c]	δ	22.4	22.4	22.4	
	$\langle\delta\rangle$[d]	21.7	21.7	21.7	
basis II[e]	δ	22.9	22.9	22.9	
	$\langle\delta\rangle$[d]	22.2	22.2	22.2	
	δ, exptl[f]	22.86	22.86	22.86	
		Cyclobutanecarbonitrile (**2**)			
basis II′	δ	21.8	27.6	20.3	126.6
	$\langle\delta\rangle$[d]	21.6	26.9	20.0	127.0
	δ, exptl[g]	22.16	27.23	19.95	122.47
		Methylcyclobutane (**3**)			
basis II′	δ	30.5	29.2	18.7	22.8
	$\langle\delta\rangle$[d]	29.7	28.2	18.3	22.8
	δ, exptl[f,h]	31.24	30.18	18.32	22.11
		(31.62)	(30.45)	(18.56)	(22.13)
		Fluorocyclobutane (**4**)			
basis II′	δ	80.2	30.7	11.6	
	$\langle\delta\rangle$[d]	80.8	30.5	12.2	
basis II	δ	79.8	30.8	11.6	
	$\langle\delta\rangle$[d]	80.4	30.6	12.2	
	δ, exptl[i]	86.49	31.10	10.54	
		Bicyclo[1.1.1]pentane (**5a**)			
basis I	δ	29.3	45.6	29.3	
basis II	δ	30.9	47.2	30.9	
	δ, exptl[j]	33.59	50.75	33.59	
		1-Cyanobicyclo[1.1.1]pentane (**6a**)			
basis I	δ	18.6	49.3	26.3	126.2
basis II′	δ	24.5	50.7	28.0	123.6
	δ, exptl[k]	27.37	53.81	31.82	117.25
		1-Methylbicyclo[1.1.1]pentane (**7a**)			
basis I	δ	26.0	47.0	27.5	13.2
basis II′	δ	38.2	48.5	26.4	19.9
	δ, exptl[l]	42.17	52.18	27.39	19.07
		1-Fluorobicyclo[1.1.1]pentane (**8a**)			
basis I	δ	58.2	48.7	17.5	
basis II′	δ	69.9	49.7	15.7	
	δ, exptl[m]	74.93	53.18	14.79	

[a] All values are in ppm. Experimental values were measured relative to TMS in chloroform-*d* solvent. [b] Calculated chemical shifts for basis I assume a TMS reference value of 217.9 ppm using the ^{13}C IGLO CH_4 shielding value of 220.2 ppm for this basis set and a CH_4 chemical shift of −2.3 ppm. [c] Same as footnote *b* except that the TMS reference value of 198.7 ppm is based on a calculated CH_4 value of 201.0 ppm. [d] The calculated chemical shift is an average of the basis set II′ shift results over the puckering potential according to eq 3. It was assumed that the incremental effects of pucker averaging for basis sets II and II′ would be the same. [e] Same as footnote *b* except that the TMS reference value of 198.3 ppm is based on a calculated CH_4 value of 200.6 ppm. [f] Reference 12. [g] Reference 6. [h] Reference 14. [i] Reference 13. [j] Reference 25. [k] Reference 26. [l] Reference 27. [m] Reference 28.

Differences (−4.6 and 6.1 ppm, respectively) between the calculated and experimental values for these two carbons are much larger than any others in this series. As noted previously, the optimized geometries for CNCB and FCB are particularly sensitive to basis set quality. It seems likely that these disparities would be partially corrected by performing the geometry optimizations with larger basis sets and by introducing the effects of electron correlation. Moreover, adequate descriptions of nitrogen and fluorine shieldings invariably require larger basis sets than the ones used here, and it appears to be generally true that shielding results for atoms bonded to these atoms are also sensitive to basis set quality. The effects of electron correlation for shielding calculations are expected to be most important for molecules having multiple bonds,[3] e.g., the nitrile function.

In Table II for cyclobutane (**1**) in the lowest energy conformation the calculated ^{13}C chemical shift (basis set II′) is 22.4 ppm in comparison with the solution experimental value of 22.86 ppm.[12] The calculated 26.1° pucker angle is several degrees smaller than the experimental gas-phase values of 28.58° and 27.9° as inferred from microwave[36] and electron diffraction[37] studies, respectively. On the basis of the angular dependence of the CB chemical shift (Section IV.B.), a 2.5° increase in the pucker angle should increase the calculated CB shift by 0.6 to 23.0 ppm, which is fortuitously in better agreement with the experimental value. An IGLO basis set II (see Table II) calculation for CB with the same geometry leads to a value of 22.9 ppm for the chemical shift. Increasing this value by 0.6 ppm to correct for the disparity in pucker angle gives a value that is not quite as good.

The low potential energy barrier (vide infra) for cyclobutane suggests that the calculated shielding values might be very sensitive to pucker angle averaging. Thus, *a major goal of this study was to investigate the importance of the ring-puckering motions on the chemical shifts of cyclobutane and the substituted cyclobutanes.* The calculated chemical shift averages $\langle\delta\rangle$ for **1**–**4** were obtained by numerical integration of eq 3 (at 300 K) over the chemical shift and puckering potential data (Section IV). The averaged chemical shifts are entered in Table II. For cyclobutane the average over the puckering motion decreases the calculated (basis set II′) result in Table II by 0.7 ppm. Because basis sets II and II′ give almost the same chemical shifts, it is reasonable to expect that pucker angle averaging would lead to almost identical results. Thus, subtracting the 0.7-ppm difference leads to an average value of 22.2 ppm (basis set II) in Table II. The agreement with the experimental result is perhaps fortuitous because gas-phase and solution experimental values often differ by several ppm. The only gas-phase chemical shift in these series of compounds appears to be the recently reported one of 30.57 ppm for cyclobutane referenced to methane.[11] The disparity with the 25.2-ppm IGLO value (basis set II isotropic shielding data for CB and methane) is probably indicative of cancellation of errors for solution values. This gas-phase ^{13}C chemical shift is closer to a calculated shift of 27.9 ppm, which can be inferred from a recent IGLO (basis set II) result in which cyclobutane had been optimized at the MP2/6-31G* level.[22c]

In Table II are entered the calculated isotropic ^{13}C chemical shifts δ (basis set II′ only) for the substituted cyclobutanes in their minimum energy conformations which have the CN, CH_3, or F substituent in equatorial positions. Averaging over the puckering potential via eq 3 leads to average values $\langle\delta\rangle$ for the ring carbons which differ from equilibrium geometry values by no more than 1.0 ppm. The overall agreement with the experimental values is still comparable. For the CN carbon, however, the increase of about 0.5 ppm is in the direction of greater shielding and an even larger difference with the experimental value. Pucker angle averaging for MECB increases the disparity with experimental values for the C1 and C2 ring carbons whereas the methyl shift appears to be unaffected by the puckering motion. For FCB in Table II the largest change on pucker angle averaging is 0.6 ppm. From the data in Table II it can be seen that the effects of pucker angle averaging are small and do not lead to meaningful improvement at this level of theory. Relatively small effects for pucker angle averaging are consistent with the angular dependencies of the energies and chemical shifts in Section IV. The potential energy profiles near the minima are essentially symmetric functions for small variations of the pucker angle, whereas the chemical shifts have opposite parity, e.g., they are monotonically increasing or monotonically decreasing functions over the same range of pucker angles. To investigate the importance of the underestimation of the barrier heights (Section IV.A), the calculated energy profiles were scaled to bring them into agreement with the experimental barrier heights, and the pucker angle averages were recalculated. These resulting averages differed from those in Table II by no more than 0.2 ppm.

Somewhat larger differences between calculated and experimental chemical shifts are noted for the four bicyclo[1.1.1]pentane molecules **5a**–**8a** in Table II. The average deviation is 2.7 ppm between calculated and experimental values for all eleven carbons not including the CN carbon of **6a** and C1 carbon of the 1-fluoro-substituted compound **8a**. Again, these carbons exhibit the largest disparities (−6.4 and 5.0 ppm, respectively) by amounts which are similar to those noted above for CNCB and FCB. In fact, except for these two carbons (and the methyl of MECB) all ^{13}C nuclei in the four series of 1-substituted bicyclo[*n*.1.1]alkanes are deshielded relative to the corresponding cyclobutane. It will be argued in a subsequent section that both shifts to high and low frequencies are strongly influenced by the combined effects of increasing ring strain and conformationally dependent substituent effects. The neglect of electron correlation effects for the energy optimized structures is also a factor in the disparity between the calculated and experimental values in Table II. In a very recent study of bicyclo[1.1.1]pentane, which had been optimized at the MP2/6-31G* level,[22c] the calculated ^{13}C chemical shifts for the C1 and C2 carbons were 32.2 and 48.8 ppm, respectively, in somewhat better conformity with the experimental values of 33.59 and 50.75 ppm.

IV. Pucker Angle Dependence of the Energies and the ^{13}C Isotropic Chemical Shifts

Ring puckering in cyclobutanes is envisioned as arising from a delicate balance between vicinal C1–C2 and transannular C1–C3 interactions.[18–22] The first of these is unfavorable for planar arrangements of the ring because these have eclipsed vicinal hydrogens. The puckering of the ring decreases not only the C–C–C angles of the ring but also the distance between the C1 and C3 groups. Both are energetically unfavorable for the puckered arrangements. Since cyclobutane and many substituted cyclobutanes have double minima in the puckering potentials, both axial and equatorial isomers occur. A number of conclusions have been drawn[20,42] from the MO calculations for representative substituted cyclobutanes: the higher the electronegativity, the greater the stability of the equatorial arrangement, and the smaller the pucker angle of the axial forms, the larger the pucker angle of the equatorial form.

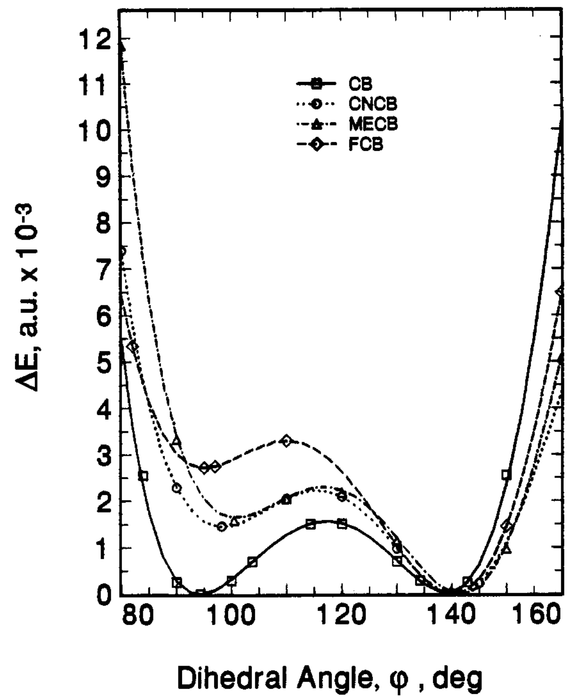


Figure 3. Energies (HF/6-31G**) of cyclobutane (**1**), cyclobutanecarbonitrile (**2**), methylcyclobutane (**3**), and fluorocyclobutane (**4**) plotted as a function of dihedral angle.

Table III. Calculated Energy Differences between Axial and Equatorial Arrangements and the Barrier Heights for Cyclobutane and the Substituted Cyclobutanes **2**–**4**[a]

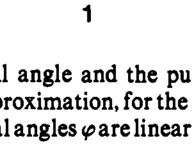
	ax – eq diff		barrier	
compd	calc	expt	calc	expt
1	0.0	0.0	339 (331[b])	510 ± 0.3,[c] 513,[b] 449 ± 0.9[d]
2	318.5	287.7,[e] 258 ± 50[f]	491	585.3[e]
3	347.4	247 ± 20[g]	507	641 ± 20[g]
4	597.8	722[h]	723	803[h]

[a] All values in cm^{-1}. [b] Reference 21. [c] Reference 37. [d] Reference 52. [e] Reference 53. [f] Reference 38. [g] Reference 54. [h] Reference 55.

A. Pucker Angle Dependence of the Energy. The energies for cyclobutane (**1**) and the substituted compounds **2**–**4**, which were obtained at the HF/6-31G** level, are plotted (CB, open squares; CNCB, open circles; MECB, open triangles; FCB, open diamonds) in Figure 3 as a function of the dihedral angles φ.[50] Dihedral angles were constrained to representative values between 80° and 160° including the angle in the energy optimized structures having axial and equatorial substituents. In the case of CB this conformation has axial and equatorial C–H bonds with 94.33° and 139.23° dihedral angles, respectively. The H–C1–C2–C3 dihedral angle φ, which is measured about the C1–C2 bond in **1**, was used in preference to the pucker angle τ to make the correspondence with previous work on the conformational dependencies of α-, β-, and γ-substituent effects on ^{13}C chemical shifts.[1,2] The dihedral angle and the pucker angle are closely related. To a good approximation, for the cyclobutane optimized geometries the dihedral angles φ are linearly related to the pucker angles τ,

$$\varphi = 0.872\tau + 116.9° \qquad (4)$$

with correlation coefficient $r^2 = 0.9995$ and standard deviation 0.52°. Thus, planar cyclobutane has a dihedral angle of 116.9°. Of course, the corresponding relationships for the three *substituted* cyclobutanes differ somewhat from eq 4,[50] but it is sometimes convenient to speak of these angles interchangeably. At or near the extreme values for the dihedral angles in Figure 3 the rings become distorted from D_{2d} (C_s for the substituted molecules) symmetries. For example, at an equatorial dihedral angle of 150° one of the C–C bond lengths is 0.002 Å longer than the other three. This leads to an 0.2 ppm average deviation in the calculated CB shieldings for the four carbons.



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The calculated energies for **1**–**4** were fit in the least-squares sense to a truncated Fourier series (eq 2), and these are plotted (solid, dotted, dot–dash, and dashed lines, respectively) in Figure 3. Double-well potentials are noted for all three substituted molecules. With the possible exception of CNCB these follow the expected trends with increasing substituent electronegativity.[20,42] In Table III the calculated potential energy barrier (339 cm^{-1}) for cyclobutane is compared with some recent experimental values. This value is substantially lower than the experimental

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(50) The numerical values of the energy for each conformation are given in Tables SI–SIV of the supplementary material. The pucker angles τ are also included for all conformations.

Table IV. Coefficients A_n of the $\cos(n\varphi)$ Terms and Constants B in the Fourier Expansions (Eq 1) for the Conformational Dependencies of the ^{13}C Isotropic Shielding of **1**–**4**[a]

	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_9	B	SD
					Cyclobutane[b]					
C1 (I)	2.44		7.21		–0.39				201.38	0.15
C1 (II′)	1.92		6.03		–0.41				174.94	0.14
					Cyclobutanecarbonitrile					
C1	–3.95		3.26		–0.72			0.38	173.46	0.06
C2	–1.64		2.70		–1.49				170.04	0.20
C3			4.60		0.39			0.50	176.41	0.06
CN	–5.53		–0.99		–0.77				69.07	0.16
					Methylcyclobutane					
C1	2.32		4.21		–0.30		–0.15	0.45	168.92	0.14
C2		1.73	5.85	2.67					169.23	0.23
C3	–0.45		5.11				–0.15	0.48	177.92	0.09
CH_3	0.96		–2.94				0.44	0.15	178.01	0.04
					Fluorocyclobutane					
C1	–3.32	2.89				0.75	0.21		115.69	0.16
C2	–6.23	–4.19	1.31				0.43		163.45	0.06
C3		4.67	2.51	–2.22	–0.96				183.98	0.15

[a] All of the ^{13}C shielding coefficients A_1 – A_9, B, and the standard deviations (SD) in the calculated σ are in ppm. All shielding data were based on linear regression of the IGLO basis set II′ results. The smallest correlation coefficient, r^2 = 0.994, occurred in the shielding data for the C2 carbon on methylcyclobutane. [b] Basis set I results are given only for cyclobutane.

values of 510 ± 3[37] and 513 ± 2[21] cm^{-1}. The calculated results for cyclobutane compare favorably with those recently reported by Champion et al.[21] in terms of a 4-21G** basis set. In general, barriers are quite sensitive to basis set quality and often require that electron correlation effects be included.[51]

Entered in Table III are the calculated energy differences in cm^{-1} between axial and equatorial arrangements and the barrier heights for each of the substituted cyclobutanes. Also included are some recent experimental values.[52-55] The expected double-well potentials are qualitatively reproduced. For CNCB and MECB the axial–equatorial energy differences are overestimated, but for FCB this quantity is underestimated by 124 cm^{-1}. In all cases the barrier heights in Table III are too small. The largest and smallest disparities of about 170 and 80 cm^{-1} occur for CB and FCB, respectively.

B. Pucker Angle Dependence of the ^{13}C Chemical Shifts. 1. Cyclobutane. The isotropic ^{13}C chemical shifts for cyclobutane (based on the IGLO basis sets I and II′ shielding data[56]) are plotted (open circles and filled squares, respectively) in Figure 4 as a function of the dihedral angle φ in the range 80 to 160°. Linear regression analyses of the shielding data produced the coefficients A_n and B in eq 1 and the lines passing through the calculated points in Figure 4. These coefficients and the standard deviations (SD) in the calculated shieldings are entered in Table IV. Basis set I ^{13}C isotropic chemical shifts, $\delta(\varphi)$, are given by the expression

$$\delta(\varphi) = -2.4 \cos \varphi - 7.2 \cos 3\varphi + 0.4 \cos 5\varphi + 16.6 \text{ ppm} \quad (5)$$

with a standard deviation of 0.15 ppm and correlation coefficient (r^2) of 0.998. For basis set II′ the analogous expression is

$$\delta(\varphi) = -1.9 \cos \varphi - 6.0 \cos 3\varphi + 0.4 \cos 5\varphi + 23.8 \text{ ppm} \quad (6)$$

(SD = 0.14 ppm, r^2 = 0.998.) Primarily, the improvement provided by this larger basis set is the increase of 6.8 ppm for the angularly independent term. As noted previously, the angular terms are less sensitive to basis set size.[1,2]

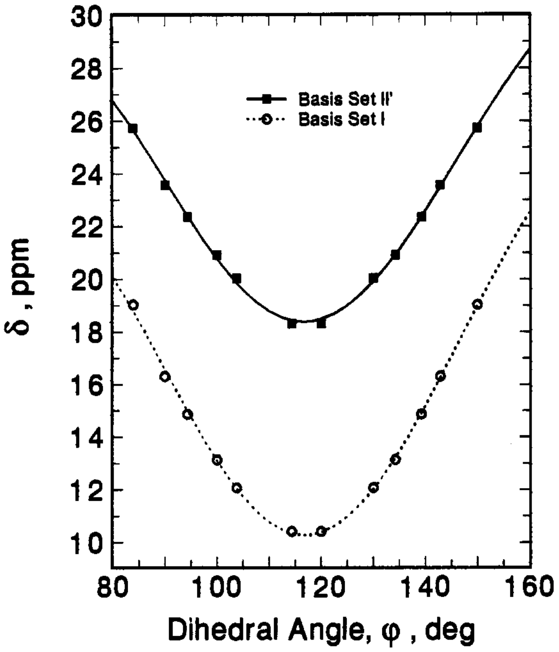

Figure 4. Calculated ^{13}C chemical shifts of cyclobutane plotted (open circles and filled squares for IGLO basis sets I and II′, respectively) as a function of the dihedral angle φ in the range 80 to 160°.

The significance of the various cosine terms in the truncated Fourier series expression for the energy conformational dependence [$E(\varphi)$ in eq 2] has been discussed by Radom, Hehre, and Pople.[57] Although there is no obvious reason that the torsional features of the shielding should parallel the energies, in some cases they are similar. For example, the calculated isotropic ^{13}C shielding in ethane is very accurately described by the 3-fold term.[1] This term corresponds to interactions between the vicinal C–H bonds which energetically favor staggered conformations. Therefore, it is probably not a coincidence for cyclobutane that these are also the most important angular terms in the pucker angle dependence of the chemical shifts (eqs 5 and 6). Since

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(56) These chemical shifts were obtained from the isotropic shielding data from Tables SI–SIV of the supplementary material.

(57) Radom, L.; Hehre, W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 2371–2381.

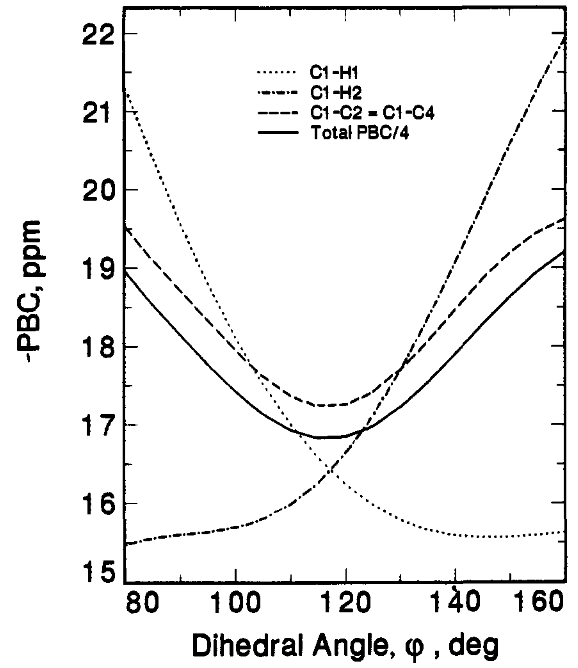

Figure 5. *Magnitudes* of the individual bond paramagnetic contributions (PBC, basis set II′) to the ^{13}C shielding in cyclobutane plotted as a function of dihedral angle.

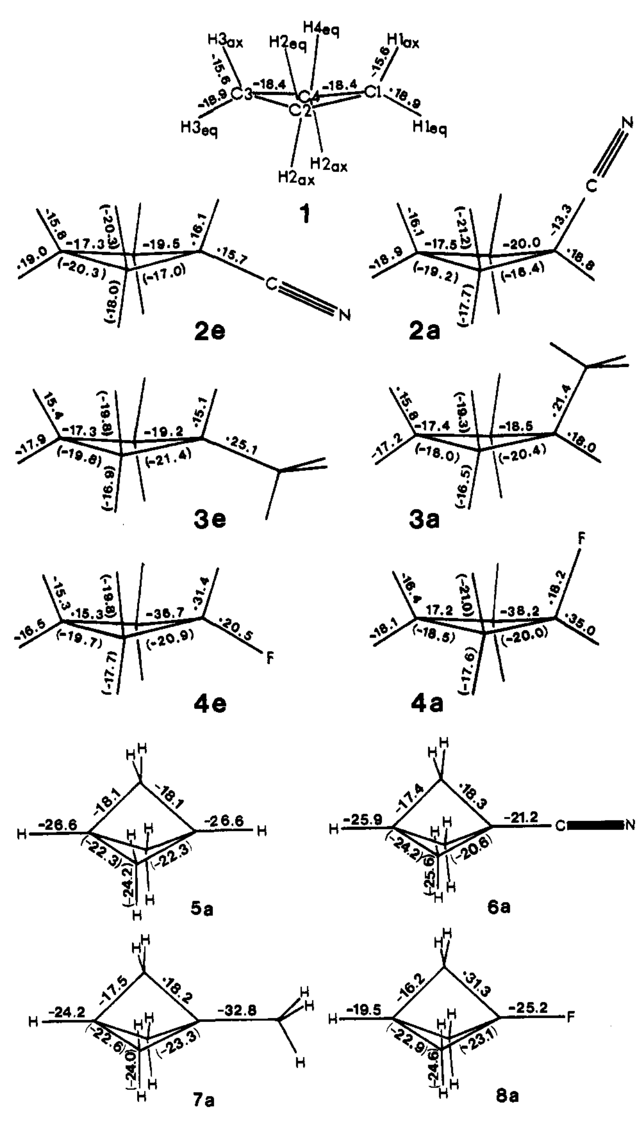

Figure 6. Paramagnetic bond contributions (IGLO basis set II′) for each of the four bonds directed to the ring carbons of (a) cyclobutane and the equatorial and axial arrangements of cyclobutanecarbonitrile (**2e** and **2a**), methylcyclobutane (**3e** and **3a**), and fluorocyclobutane (**4e** and **4a**) and (b) the bicyclo[1.1.1]pentanes **5a**–**8a**. The PBC's for the C2 carbons are given in parentheses.

3-fold terms are symmetrical about $\varphi = 120°$, the relative minimum in the chemical shift occurs for nearly planar cyclobutane. The only other important angular terms in eqs 5 and 6 are the 1-fold terms. Radom et al.[57] ascribed 1-fold terms to local dipole or steric interactions at the two ends of the molecule. Presumably, for CB these are the transannular CH_2 interactions. In Section V it will be seen that 1-fold cosine terms play an important role for the angular dependence of substituent effects.

From the IGLO studies of ^{13}C shielding in hydrocarbons[1,3,44,45] it has been shown that the most important *conformational changes* in the total ^{13}C shielding arise from paramagnetic contributions for the four bonds (localized MO's) on carbon. In an attempt to sort out the electronic factors which are responsible for the pucker angle effects in CB and the substituted cyclobutanes, local paramagnetic shielding contributions (PBC's) associated with each of the bonds were examined as a function of the dihedral angle. All of the paramagnetic bond contributions to the cyclobutane ^{13}C shielding (basis set II′) are negative in sign; plotted in Figure 5 are the *absolute magnitudes* of the individual PBC's so that the curves will have the same sense as the chemical shifts in Figure 4. The four curves in Figure 5 were based on linear regression analyses of the computed PBC's. The axial (equatorial) C–H bonds become equatorial (axial) as the molecule passes through the planar orientation at $\varphi = 116.9°$ in Figure 5. The PBC's for *axial* C–H bonds vary by less than 1 ppm over a 40° dihedral angle range while those for the *equatorial* C–H bonds change by more than five times this much! Thus, the PBC's for *equatorial bonds dominate the conformational dependencies* of the ^{13}C chemical shifts. For example, experimental results in Table II show that the C1 carbon of bicyclo[1.1.1]pentane **5a** is 10.7 ppm to high frequency (lower field) of cyclobutane. A substantial part of this deshielding is attributable to the increasing PBC magnitude for the exocyclic C–H bond as the pucker angle increases. This can be seen from the calculated PBC's for the CNCB ring carbons in Figure 6a and for bicyclo[1.1.1]pentane-1-carbonitrile (**5a**) ring carbons in Figure 6b. For the equatorial C–H bonds of cyclobutane (**1**) and the C1–H bond of bicyclo[1.1.1]pentane **5a**, the calculated paramagnetic bond contributions are about −19 and −27 ppm, respectively. Thus, the change in the contribution from this bond alone accounts for almost 80% of the deshielding of the C1 carbon relative to cyclobutane. In contrast, the much larger (ca. 28 ppm) shift for the C2 carbon of **5a** compared to cyclobutane is due to the substantial increases in the PBC magnitudes for all four bonds. The patterns of increasing PBC magnitudes in Figure 6a,b and decreasing bond lengths in Figures 1 and 2 suggest similar origins for both.

2. Cyclobutanecarbonitrile. Calculated (IGLO basis set II′) ^{13}C chemical shifts[56] for the ring carbons and the CN (C5) carbon of the cyclobutanecarbonitrile **2** are plotted in Figure 7, parts a and b, respectively, as a function of the dihedral angle φ(C5–C1–C2–C3).[58] The C1, C2(C4), and C3 shifts are represented in Figure 7a by filled squares, filled circles, and filled triangles, respectively. The nitrile carbon shifts are denoted by open circles in Figure 7b. Because unsymmetrical ring distortions led to a slight nonequivalence of the C2 and C4 carbons at dihedral angles of 80° and 145°, the CNCB shifts cover this smaller range in the figures. Calculated chemical shifts for an energy optimized CNCB structure (HF/6-311G** level[59]) with $\varphi = 149°$ followed the same shielding trends but, for consistency, these data were not used in the regression analyses.

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(58) In the figures the solid lines through the calculated data were based on regression analysis with coefficients for eq 1 given in Table IV. All of the figures were plotted for dihedral angles in the range 80° to 160°.

(59) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.

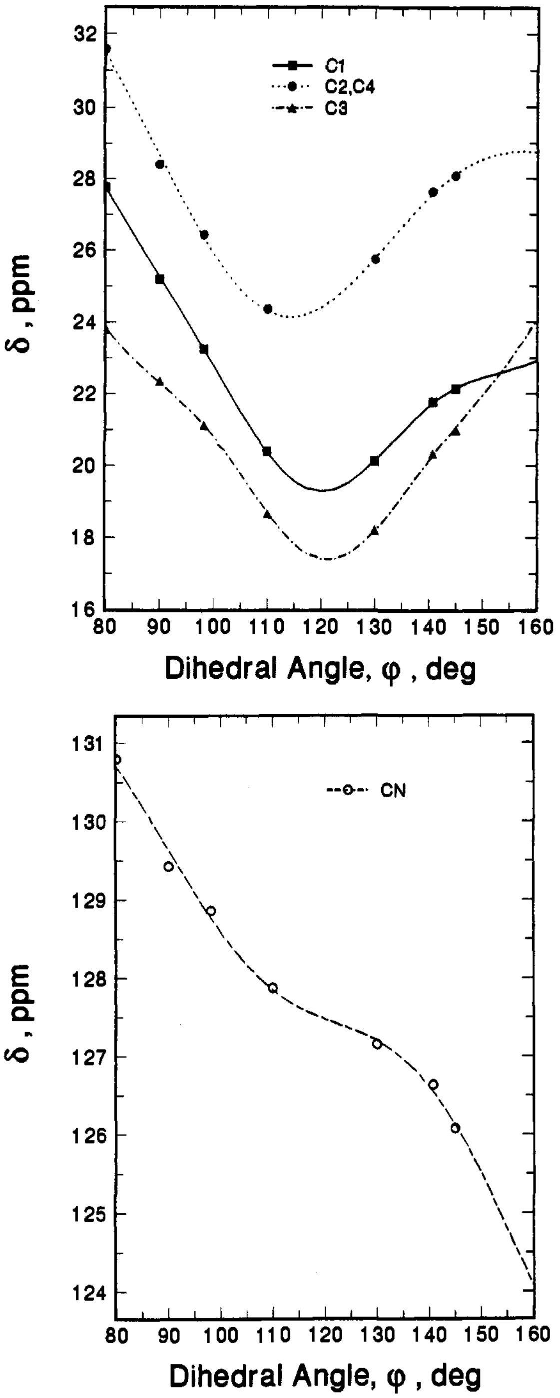


Figure 7. (a, top) Calculated (IGLO basis set II′) ^{13}C chemical shifts for the ring carbons of the cyclobutanecarbonitrile **2** plotted as a function of the dihedral angle φ(C5–C1–C2–C3). The C1, C2(C4), and C3 shifts are represented by filled squares, filled circles, and filled triangles, respectively. (b, bottom) Calculated (IGLO basis set II′) ^{13}C chemical shifts for the CN carbon of cyclobutanecarbonitrile (**2**) plotted as a function of the dihedral angle φ.

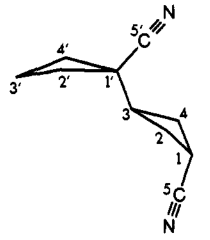
For each of the CNCB ring carbons the ^{13}C chemical shifts have minima near the planar arrangements in Figure 7a. Not unexpectedly, replacing a cyclobutane hydrogen by a nitrile group skews the curves. For small dihedral angles the nitrile is closer to the C3–H bond, whereas for larger dihedral angles C1–H and C3–H are proximate. In contrast to the ring carbons, which are most shielded near the planar arrangements, the calculated nitrile carbon shifts in Figure 7b decrease monotonically with dihedral angle. Because there are no vicinal C–H interactions as for the ring carbons, the 3-fold cosine term (which has an extremum at 120°) is no longer a major factor.

Table V. Estimated ^{13}C Chemical Shifts for 1-Substituted Cyclobutanes and Bicyclo[*n*.1.1]alkanes Compared with the Experimental Values[a]

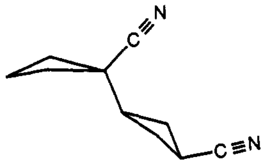
	C1		C2,C4[b]		C3[b]		C5	
	expt	est[c]	expt	est[c]	expt	est[c]	expt	est[c]
			Bicyclo[*n*.1.1]alkanes[d]					
5c	34.2		33.3		34.2			
5b	39.5		39.0		39.5			
5a	33.5		50.8		33.5			
			1-Carbonitrile Compounds					
9t[e]	18.5		28.5		38.5		122.5	
9c[e]	17.2		29.2		38.0		120.8	
6c[f]	32.0	31.5	36.8	36.6	31.3	30.7	125.8	124.9
6b[f]	35.1	33.7	42.2	38.9	38.3	34.9	120.8	124.0
6a[f]	27.4	26.4	53.8	47.7	31.8	30.0	117.2	122.3
			1-Methyl- and Dimethyl-Substituted Compounds					
10t[g]	26.1	26.0	36.4	31.8	26.1	26.0	22.0	22.7
10c[g]	26.9	26.2	38.5	34.8	26.9	26.2	22.5	22.8
11[g]	35.9	36.0	34.9	33.0	14.8	14.7	29.4	–
7c[h]	39.7	40.9	38.8	38.0	30.1	29.2	28.0	21.6
7b[h]	48.5	44.6	43.8	40.8	36.7	33.4	19.8	19.6
7a[h]	42.2	38.5	52.2	50.4	27.4	28.0	19.1	19.3
			1-Fluoro-Substituted Compounds					
8c[i]	93.8	88.7	39.7	39.6	25.0	21.1		
8b[i]	95.2	88.5	43.1	43.2	27.1	23.7		
8a[i]	74.9	78.4	53.2	54.4	14.8	16.0		

[a] All values in ppm. [b] For the ring carbons of bicyclo[3.1.1]heptanes and bicyclo[2.1.1]hexanes this numbering is unconventional. [c] Estimated values for carbon shifts in the substituted bicyclic molecules **6c**–**8c**, **6b**–**8b**, and **6a**–**8a** are from the bicyclo[*n*.1.1] alkane **5a**–**5c** data and the angularly dependent substituent shifts in Table VI. [d] Reference 25. [e] Reference 6. [f] Reference 26. [g] Reference 12. [h] Reference 27. [i] Reference 28.

Since the ^{13}C chemical shifts of both the ring and CN carbons of cyclobutanecarbonitrile are largely determined by the ring pucker angle, these provide an excellent probe of stereochemistry in oligomers and polymers having all CNCB rings in the backbone.[7,60] For example, *trans*-3-(1′-cyanocyclobutyl)cyclobutane-1-carbonitrile dimer (**9t**) is clearly distinguished from the corresponding *cis* dimer **9c** via the ^{13}C chemical shifts for the 1,3-fused rings. These ^{13}C chemical shifts are included in Table V. Energy optimized structures (HF/3-21G)[61] show that the 1,3-fused ring in **9t** has an equatorial cyanocyclobutyl group and an axial nitrile with φ = 95.6°. The 1,3-fused ring of the *cis* dimer **9c** has both groups equatorial and a dihedral angle of 138.4° for the nitrile. The experimental chemical shift *differences* for the C1, C2, C3, and C5(CN) carbons in Table V are 1.3, –0.7, 0.5, and 1.7 ppm, respectively. Because the cyanocyclobutyl groups at C3 are equatorial in both isomers, these differences primarily reflect chemical shift changes for an axial versus an equatorial nitrile. In comparison, the differences in the calculated CNCB chemical shifts at these two angles are 2.4, –0.2, 1.7, and 2.3 ppm, respectively. The results are not in quantitative



9t



9c

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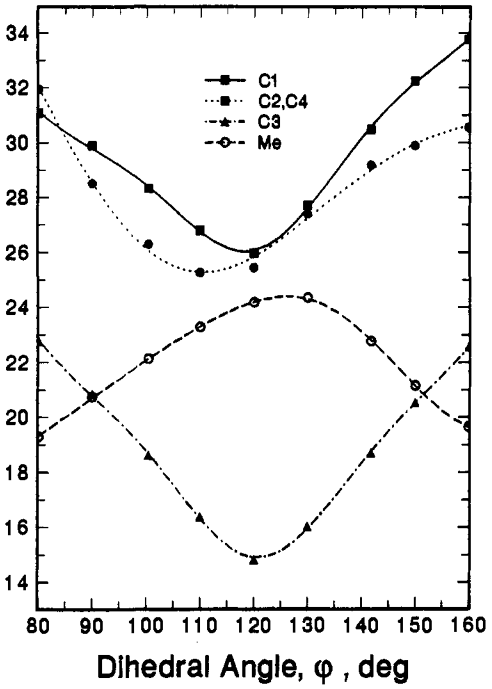

Figure 8. The IGLO ^{13}C chemical shift results for methylcyclobutane (**3**) are plotted as a function of the dihedral angle φ(C5–C1–C2–C3). The C1, C2(C4), C3, and CH_3 shifts are represented by filled squares, filled circles, filled triangles, and open circles, respectively.

agreement, but they are close enough to verify the ring stereochemistries.

In Figure 7a,b the magnitudes of slopes of the chemical shifts for the ring and nitrile carbons are 0.1–0.2 ppm/deg near the axial and equatorial nitrile orientations. It is tempting to propose that the triad and pentad fine structure of this magnitude in the polymer spectra[7] reflect 1–2° changes in the ring pucker angles. However, in the 1,3-fused bicyclobutane oligomers,[6,7] factors such as the importance of disubstitution and internal rotation[60] cannot be discarded.

Depicted in Figure 6a for axial and equatorial cyclobutanecarbonitrile are the paramagnetic bond contributions (PBC's) for the four localized bonds of each of the ring carbons (PBC's for the C2 carbon are given in parentheses). Analogous data for bicyclo[1.1.1]pentane-1-carbonitrile (**6a**) are given in Figure 6b. The PBC's for equatorial bonds are more negative than for axial bonds (typically, in **2a** and **2e** these are 3–4 ppm more negative). The PBC for the exocyclic C1–C bond of **6a** is an additional 5.5 ppm more negative. Clearly, this pattern of increasing PBC magnitudes with increasing pucker angle parallels the trends to shorter bond lengths in Figures 1 and 2. The PBC data also show which bonds are most affected by the substituent and pucker angle. For example, the near equality of the chemical shifts for the C1 carbon in CNCB and CB occurs because of compensating changes in the four PBC's at C1. However, the C3 resonance of CNCB occurs at a slightly lower frequency (higher field) than for CB because the PBC's for the C2–C3 and C3–C4 bonds of **2e** are each about 1 ppm more positive. From Figure 6a it can be seen that the major effect of an approximate 40° increase of the pucker angle for **6a** is a 5.5-ppm increase in the magnitude of the PBC for the exocyclic C–C bond. This is clearly the dominant term in the 5.1-ppm shift of the C1 carbon to higher frequency. All four of the PBC's are substantially more negative for the C2 carbon of **6a** than for the C2 carbon of **2e**. These are the most important terms leading to the large (23.6 ppm) shift of the C2 carbon to higher frequency.

3. Methylcyclobutane. The IGLO ^{13}C chemical shifts[56] for methylcyclobutane (**3**) are plotted in Figure 8 as a function of the dihedral angle φ(C5–C1–C2–C3) in the range 80–160°. The C1, C2(C4), C3, and CH_3 shifts are represented by filled squares, filled circles, filled triangles, and open circles, respectively.[58] In contrast to the ring carbon shifts which exhibit "normal" relative minima near the planar rings, the methyl carbon ^{13}C shift profile is inverted.

The calculated ^{13}C chemical shifts in Figure 8 are consistent with the experimental data for several disubstituted cyclobutanes in Table V.[12] Observed ^{13}C chemical shifts for *trans*-1,3-dimethylcyclobutane (**10t**), *cis*-1,3-dimethylcyclobutane (**10c**), and 1,1-dimethylcyclobutane are entered in Table V.[12] The energy optimized structure[61] (HF/6-31G** level) for **10t** has both axial (φ = 100.0°) and equatorial (138.4°) methyl groups, whereas **10c** has both methyl groups equatorial (141.9°). For 1,1-dimethylcyclobutane (**11**) the methyl group dihedral angles are 97.1 and 134.4°.[61] *Estimated* ^{13}*C* chemical shifts for the C1-(C3) and C2 ring carbons of **10t**, **10c**, and **11** in Table V were based on the calculated results for methylcyclobutane at these dihedral angles and the α-, β-, and γ-substituted increments (Section V.A) for the second methyl group. The estimated value for the *trans* compound additionally reflects an average over conformations with axial and equatorial methyls. The results based on these transferability assumptions in Table V are in good agreement with the experimental data. The only exceptions are for the C2 carbons in **10t** and **10c**. In the latter case, for example, at least half of the disparity can be traced to the previous 1–2 ppm underestimate for methylcyclobutane (Table II).

In Figure 8 the shape of the curve for the methyl carbons suggests that axial and equatorial methyls should have approximately the same chemical shifts. In fact, the experimental chemical shift data in Table V show that the methyl (C5) carbon of *trans*-1,3-dimethylcyclobutane (**10t**) is only 0.5 ppm to low frequency of that in the *cis* isomer **10c**.[12] On the basis of the angularly dependent data for MECB (Table IV) and ignoring any possible δ-substituent effects, the axial methyl in **10t** is predicted to be 1.3 ppm more shielded than the equatorial methyl. However, averaging the shifts for axial and equatorial conformations gives 22.7 ppm. This is only slightly smaller than the 22.8 ppm estimated for the methyl carbons in **10c**. These values are in reasonable correspondence with the experimental values of 22.0 and 22.5 ppm, respectively.

The experimental ^{13}C chemical shift for the C1 carbon of 1-methylbicyclo[1.1.1]pentane (**7a**) is 15 ppm to high frequency of the corresponding 1-carbonitrile **6a**. The PBC data for the bicyclic compounds in Figure 6b show that the major difference occurs in the exocyclic C–CH_3 for which the PBC is about 12 ppm more negative than the PBC for the C–CN bond.

4. Fluorocyclobutane. The IGLO ^{13}C chemical shifts[56] for the C1 carbon (filled squares) are plotted in Figure 9a versus the dihedral angle φ(F–C1–C2–C3) in the range 60–180°.[58] In contrast to the results for all of the other ring carbons which have relative minima near the planar arrangements, the C1 chemical shift of fluorocyclobutane decreases monotonically over the whole range of dihedral angles. The chemical shift curve (filled circles) for the C2 carbon in Figure 9b is also unusual in this series in having a very shallow minimum near 110°. On the other hand, the minimum (near 135°) in the chemical shift curve for the C3 carbon (filled triangles) is shifted in the opposite direction. Because the slopes of chemical shift curves in Figure 9a,b differ so much from the symmetrical curves for cyclobutane in Figure 4, it will be seen in the next section that the substituent effects of a fluorine are much larger than those for –CN or –CH_3 substituents.

The C1 carbon shielding curve of FCB has a negative slope over the whole range of angles in Figure 9a. For dihedral angles greater than 120–130° this is just the opposite to the other ring carbon chemical shifts, and it indicates that the effect of increasing the pucker angle will shift the C1 carbon to lower frequency (higher field). In fact, the experimental chemical shift data in

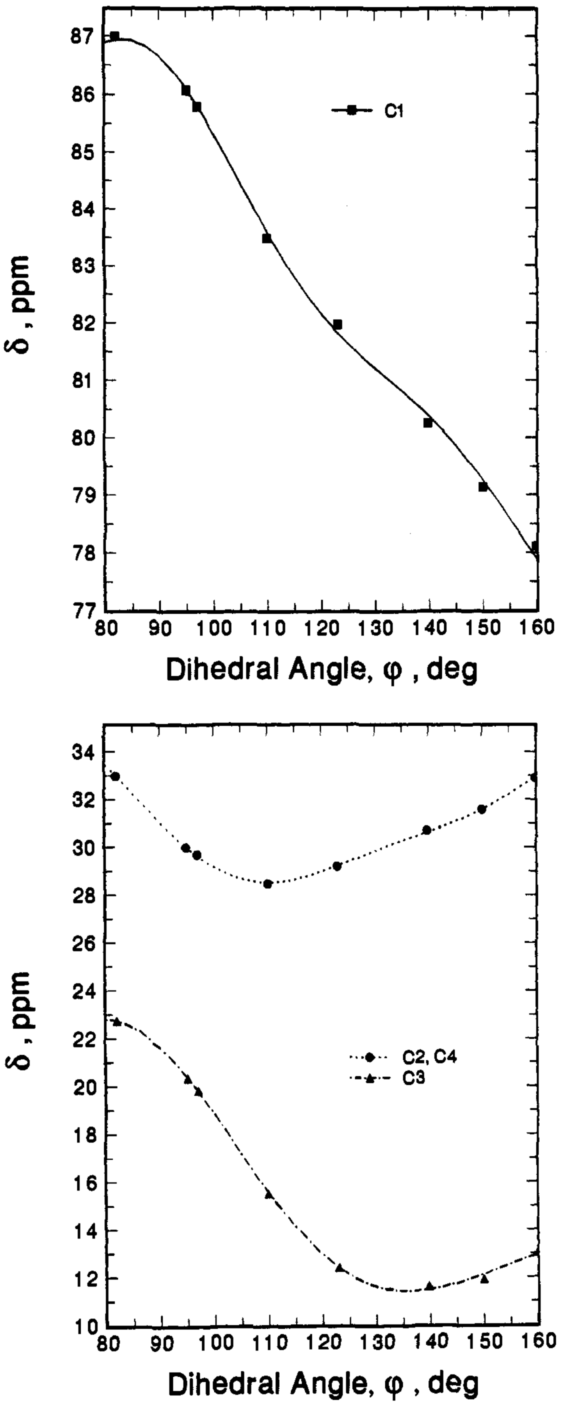

Figure 9. (a, top) The IGLO ^{13}C chemical shift results for the C1 carbon (filled squares) of fluorocyclobutane (**4**) plotted as a function of the dihedral angle φ(F–C1–C2–C3). (b) The IGLO ^{13}C chemical shift results for the C2 carbon (filled circles) and the C3 carbon (filled triangles) of fluorocyclobutane (**4**) plotted as a function of the dihedral angle φ.

Table II show that the C1 carbon in 1-fluorobicyclo[1.1.1]pentane (**8a**) is the only bicyclic *ring carbon* which is shielded (by about 12 ppm) relative to the corresponding substituted cyclobutane. In this case, however, from Figure 6a,b it can be seen that the PBC for the C1–F bond in **8a** is not unusual in being about 5 ppm more negative than that for the C1–F bond of FCB. This would lead to a shift to higher frequency, but it is more than offset by the three C–C bonds in the rings, each of which are at least 5 ppm more positive than those for the analogous bonds of FCB.

V. Substituent and Pucker Angle Effects

The α-, β-, and γ-substituent effects[4] in the ^{13}C NMR spectra of aliphatic and alicyclic compounds have played a major role in structural and conformational studies.[62] However, empirical additivity relationships[4,63,64] have little applicability for *strained cyclic molecules*. The origin of the angularly dependent γ-effects has been a subject of considerable interest,[65–70] but the usual interpretation in terms of a steric interaction model[65] appears to be inconsistent with the results in substituted cyclobutanes.[12,15] In Section V.A. is presented a discussion of α-, β-, and γ-substituent effects in the substituted cyclobutanes over a range of dihedral angles. The calculated results are compared with the substituent effects inferred from a series of substituted cyclobutanes and 1-substituted bicyclo[*n*.1.1]alkanes.

The complex chemical shift trends in the ^{13}C NMR spectra of multicyclic molecules[71] are usually analyzed in terms of empirical substituent factors which do not include conformational effects in any systematic way. Recent calculations (ab initio IGLO method) of the conformational dependence of γ-effects in model hydrocarbons satisfactorily reproduce the experimental trends in unstrained bicyclic molecules.[2] It is of interest here to examine the role of increasing ring strain on the ^{13}C chemical shifts in 1-substituted bicyclic molecules which include the cyclobutane moiety. Entered in Table V are the experimental ^{13}C chemical shifts within the four-membered rings of bicyclo[1.1.1]pentane (**5a**), bicyclo[2.1.1]hexane (**5b**), and bicyclo[3.1.1]heptane (**5c**). The cyclobutane ring pucker angle and strain decrease monotonically in this series,[24–28] having H–C1–C2–C3 dihedral angles (HF/6-31G**) of 180.0, 160.5, and 147.7°, respectively.[61] Also included in Table V are the observed ^{13}C chemical shifts for the four-membered rings in the 1-substituted bicyclic compounds with –CN, –CH_3, and –F substituents. The C2 chemical shifts are the only ones which change monotonically with increasing strain in the four-membered rings. A qualitative picture invoking additivity arguments could view the shifts as a combination of ring puckering (strain) effects in the cyclobutane rings and substituent effects from the –CH_2–, –C_2H_4–, and –C_3H_6– bridges outside the cyclobutane moiety. Of course, this leads to exactly the same results as the model based on α-, β-, and γ-substituent effects. The latter will be used in Section V.B. to estimate the ^{13}C chemical shifts in these series of bicyclic molecules.

A. α-, β-, and γ-Effects in Substituted Cyclobutanes. From the data for cyclobutanecarbonitrile and cyclobutane in Table IV, the conformational shift dependencies of a nitrile substituent are given by the expressions

$$\Delta\delta_\alpha = 5.9 \cos \varphi + 2.8 \cos 3\varphi + 0.3 \cos 5\varphi - 0.4 \cos 9\varphi + 1.5 \text{ ppm} \quad (7a)$$

$$\Delta\delta_\beta = 3.6 \cos \varphi + 3.3 \cos 3\varphi + 1.1 \cos 5\varphi + 4.9 \text{ ppm} \quad (7b)$$

$$\Delta\delta_\gamma = 1.9 \cos \varphi + 1.4 \cos 3\varphi - 0.8 \cos 5\varphi - 0.5 \cos 9\varphi - 1.5 \text{ ppm} \quad (7c)$$

Since all odd cosine terms vanish for $\varphi = 90°$, the constant terms in eqs 7a–c are roughly the α-, β-, and γ-effects of an axially oriented nitrile. The contributions from the 1-fold cosine terms are very small near axial arrangements and become increasingly negative as φ approaches 180°. Equations 7a–c are plotted in

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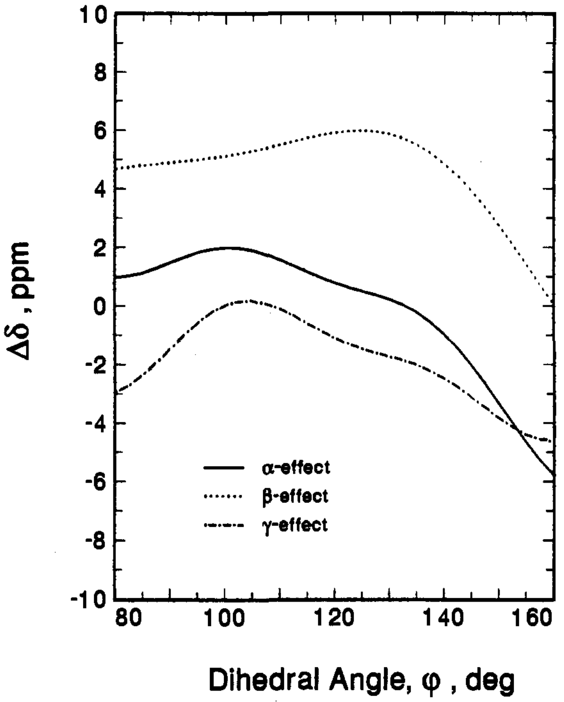

Figure 10. Conformational dependencies of the α-, β-, and γ-substituent effects (solid, dashed, and dot-dash lines, respectively) in cyclobutanecarbonitrile (**2**) plotted as a function of the dihedral angle φ.

Figure 10 (solid, dotted, and dot-dash lines, respectively) as a function of the dihedral angle φ in the range 80–160°. For cyclobutane in Figure 4 the effects of increasing dihedral angle/ring strain are deshielding. The introduction of a substituent (for example, –CN in Figure 7) has the effect of flattening out the chemical shift curves. As a consequence, most of the substituent effect curves are inverted relative to those for chemical shifts. In Figure 10 the solid curve, which depicts the α-effect of a nitrile group, has a maximum value of about 2 ppm near the axial arrangement, vanishing near the equatorial arrangement and becoming large and negative with increasing dihedral angle. The β-effects are of larger magnitude reaching a maximum near 130° and becoming negative for dihedral angles greater than about 160°. The γ-effect curve in Figure 10 has a maximum value which is slightly positive near the axial arrangement. The curve decreases to about -5 ppm for large values of the dihedral angle.

It was of interest to investigate the applicability of the predicted nitrile substituent dependencies to other cyclic molecules containing the cyclobutane rings. Entered in Table VI are values of α-, β-, and γ-effects inferred from the experimental results for a number of molecules having the cyclobutanecarbonitrile moiety. This includes the 1-substituted bicyclo[*n*.1.1]alkane-1-carbonitriles **6a–c** where dihedral angles are optimized values for the parent compounds.[61] The estimated α-, β-, and γ-substituent effects in Table VI were obtained from eqs 7a–c with these dihedral angles. In the absence of any straightforward substituent data for axial nitriles, the first entry in Table VI was simply obtained by adding the axial – equatorial differences (Section IV.B.2) between **9t** and **9c** to the values for equatorial CNCB (**2e**). For those entries in Table VI having dihedral angles less than 148°, the average deviation between the experimentally inferred values and the estimated values is 0.6 ppm. More important, the trends to more negative values (including an angle dependent sign change for the nitrile α-effect) qualitatively follow for the α- and β-substituent effects while the γ-effects are not as clear. The substantial divergence noted for larger angles is not surprising since eqs 7a–c were based on calculated CNCB data which only extended to 145°. For example, for a 180° dihedral angle eq 7a gives an α-substituent effect of -12.7 ppm in comparison with an experimental value of -6.1 ppm.

From the data in Table IV for methylcyclobutane and cyclobutane it follows that the conformational dependencies of the α-, β-, and γ-effects of a methyl substituent are given by the expressions

$$\Delta\delta_\alpha = -0.4 \cos \varphi + 1.8 \cos 3\varphi - 0.1 \cos 5\varphi + 0.2 \cos 7\varphi - 0.4 \cos 9\varphi + 6.0 \text{ ppm} \quad (8a)$$

$$\Delta\delta_\beta = -1.7 \cos 2\varphi + 0.2 \cos 3\varphi - 2.7 \cos 4\varphi + 5.7 \text{ ppm} \quad (8b)$$

$$\Delta\delta_\gamma = 2.4 \cos \varphi + 1.0 \cos 3\varphi - 0.4 \cos 5\varphi + 0.2 \cos 7\varphi - 0.5 \cos 9\varphi - 3.0 \text{ ppm} \quad (8c)$$

These expressions are plotted (solid, dotted, and dot-dash lines, respectively) as a function of the dihedral angle φ in Figure 11. In addition to the methylcyclobutane data in Table VI there are a number of entries for α-, β-, and γ-effects in molecules containing the methylcyclobutane moiety. Eliel and Pietrusiewicz investigated the ^{13}C NMR spectra of cyclobutane and seven methylated derivatives and noted that the sign and magnitude of the γ-effect for (equatorial) cyclobutanes were about the same as that for axial methylcyclohexane, suggesting that γ-effects in cyclobutanes are not associated with the usual steric compression model.[65] From the experimental data for **10t** and **11** it is possible to arrive at estimates of α-, β-, and γ-substituent effects of an axial methyl group in Table VI. However, this requires the assumptions of shift transferability. Averaging of axial and equatorial methyl effects in **10t** leads to ambiguous results for α- and γ-substituent effects, so these do not appear in Table VI.

In Figure 11 the calculated α-effects associated with a methyl group are expected to have relative maxima of about 8 ppm near both the axial and equatorial arrangements and then decrease monotonically with increasing dihedral angle. For dihedral angles greater than about 140° the experimentally inferred α-substituent effects in Table VI are relatively independent of dihedral angle whereas eq 8a implies slowly decreasing magnitudes. The calculated β-effects in Figure 11 are similar to those for CN reaching a maximum near 130° and then dropping off rapidly and possibly becoming negative for dihedral angles greater than 160°. Experimental values in Table VI for methyl β-substituent effects are consistent with the predicted maximum. The shape of the γ-effect curve for MECB is similar to that for CNCB, but it is displaced by about -2 ppm. With the exception of the value for 1-methylbicyclo[2.1.1]hexane, the experimental data imply more negative values for dihedral angle greater than 97°.

From the data in Table IV for FCB and CB it follows that the conformational dependencies of the α-, β-, and γ-effects of a fluoro substituent are given by the expressions

$$\Delta\delta_\alpha = 5.2 \cos \varphi - 2.9 \cos 2\varphi + 6.0 \cos 3\varphi - 0.4 \cos 5\varphi - 0.8 \cos 6\varphi - 0.2 \cos 7\varphi + 59.3 \text{ ppm} \quad (9a)$$

$$\Delta\delta_\beta = 8.2 \cos \varphi + 4.2 \cos 2\varphi + 4.7 \cos 3\varphi - 0.4 \cos 5\varphi - 0.4 \cos 7\varphi + 11.5 \text{ ppm} \quad (9b)$$

$$\Delta\delta_\gamma = 1.9 \cos \varphi - 4.7 \cos 2\varphi - 3.5 \cos 3\varphi + 2.2 \cos 4\varphi + 1.0 \cos 5\varphi - 9.0 \text{ ppm} \quad (9c)$$

The α- and γ-effects of a fluorine are expected to have maxima of about 59 and -2 ppm near the axial arrangements, respectively, and then drop off rapidly with increasing dihedral angle as shown in Figure 12 by the solid line and dot-dash lines, respectively. The β-effect of a fluorine has a maximum near 120° and drops off more slowly for increasing dihedral angles (dotted line in Figure 12). The experimental substituent effect data for the fluoro-substituted compounds in Table VI decrease monotonically with dihedral angle. The only exception is a value for the γ-effect in **8c**. The better correspondence between the estimated and experimental results must be attributable to the dominance of

Table VI. Experimentally Inferred Values of α-, β-, and γ-Effects for a Series of Multicyclic Hydrocarbons Compared with the Estimated Values for the Substituted Cyclobutanes

		$\Delta\delta_\alpha$			$\Delta\delta_\beta$			$\Delta\delta_\gamma$		
	dihedral angle	expt[a]	calc[b]	est[c]	expt[a]	calc[b]	est[c]	expt[a]	calc[b]	est[c]
				1-Carbonitrile Compounds						
9t	95.6[d]	0.6		1.3	3.7		4.5	−2.4		−0.9
2	140.8[e]	−0.7	−1.1	−1.1	4.4	4.8	4.7	−2.9	−2.5	−2.6
6c	147.7[f]	−2.2		−3.0	3.5		3.4	−2.9		−3.5
6b	160.5[f]	−4.4		−8.0	4.2		0.3	−1.2		−4.1
6a	180.0[f]	−6.1	−6.4	−12.7	3.1	3.5	−2.5	−1.7	−2.9	−2.1
				1-Methyl-Substituted Compounds						
11	97.1[e]	4.7		7.3	4.7		5.1	−3.5		−2.2
10t	100.0[e]	g		7.7	5.2		5.4	g		−2.0
3	141.8[e]	8.4	7.4	7.4	7.3	5.8	5.8	−4.5	−4.4	−4.4
7c	147.7[f]	5.5		6.7	5.4		4.6	−4.1		−5.0
7b	160.5[f]	9.0		5.1	4.8		1.8	−2.8		−6.1
7a	180.0[f]	8.7	7.3	5.0	1.4	1.3	−0.4	−6.1	−4.5	−5.5
				1-Fluoro-Substituted Compounds						
4	140.1[e]	63.6	57.7	57.7	8.2	8.0	8.0	−12.3	−11.2	−11.2
8c	147.7[f]	59.6		54.5	6.4		6.3	−9.2		−13.1
8b	160.5[f]	55.7		49.0	4.1		4.2	−12.4		−15.8
8a	180.0[f]	41.4	39.0	45.0	2.4	2.5	3.6	−18.7	−15.2	−17.5

[a] Differences in the experimental values of the compound and the parent compound. Since 1,1-dimethylcyclobutane has an axial and an equatorial methyl, the values entered here as the differences are referred to methylcyclobutane for which the equatorial methyl has just about the same dihedral angle. [b] Differences in the IGLO basis set II′ values for this compound and the parent compound. [c] Values deduced from the calculated angular dependencies for cyclobutane and the substituted cyclobutanes. [d] Dihedral angle from the energy optimized structure (HF/3-21G) of *trans*-3-(1-cyanocyclobutyl)cyclobutane-1-carbonitrile (**9t**).[58] [e] Energy optimized value at the HF/6-31G** level. [f] Value inferred for the energy optimized HF/6-31G** structure for the parent compound. [g] These values could not be uniquely determined.

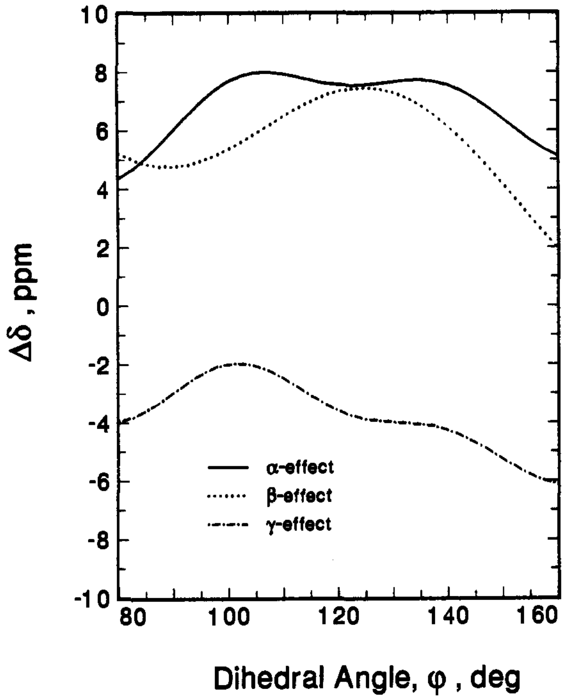

Figure 11. Conformational dependencies of the α-, β-, and γ-substituent effects (solid, dashed, and dot-dash lines, respectively) in methylcyclobutane (**3**) plotted as a function of the dihedral angle φ.

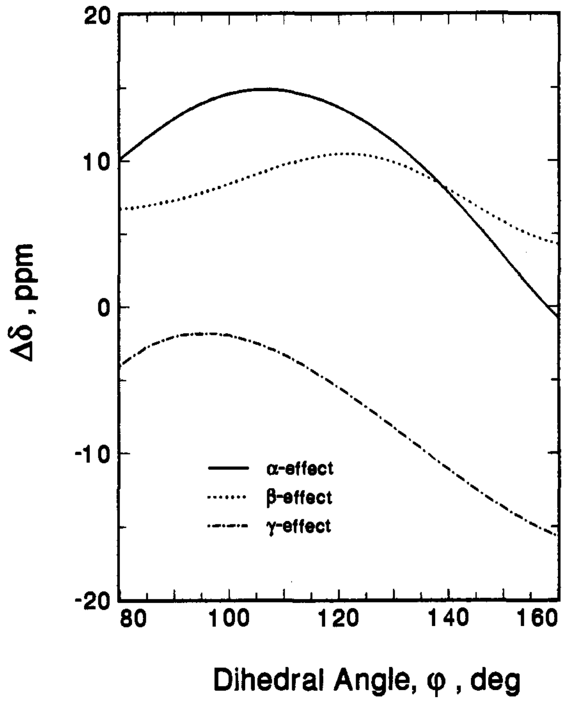

Figure 12. Conformational dependencies of the α-, β-, and γ-substituent effects (solid, dashed, and dot-dash lines, respectively) in fluorocyclobutane (**4**) plotted as a function of the dihedral angle φ.

fluorine substituent effects. In fact, extrapolation of the FCB data (eqs 9a–c) to a dihedral angle of 180° leads to only a 2 ppm average deviation for all three α-, β-, and γ-effects in **8a**.

B. Pucker Angle Dependence of the Chemical Shifts in the 1-Substituted Bicyclo[*n*.1.1]Alkanes. Entered in Table V are the experimental ^{13}C chemical shifts for the bicyclo[*n*.1.1]alkanes **5a–c**, where *n* = 1, 2, 3, and the corresponding 1-substituted compounds **6a–c**, **7a–c**, and **8a–c**. The ^{13}C chemical shifts for all of these substituted molecules were estimated by adding the appropriate α-, β-, and γ-substituent data from Table VI to the chemical shifts of the parent molecules. The equatorial C1–H bonds were used as the criterion for the pucker angle rather than the axial $C1–C_m$ bond because the latter are relatively insensitive (for example, see Figures 5 and 6) to the effects of ring puckering.

The estimated ^{13}C chemical shifts for the ring carbons in bicyclo[3.1.1]heptane-1-carbonitrile (**6c**) in Table V are within 0.6 ppm of the experimental data. In this case the assumed 147.7° dihedral angle is close to the maximum angle for the CNCB calculations. Since the dihedral angles for **6a** and **6b** are substantially larger, the disparities of several ppm are expected. Qualitative consistency is achieved with all of the experimental data. Also included in Table V are estimates of the CN carbon shifts. These are simply the nitrile shifts for the three angles using the CNCB data in Table IV. Although the calculated values differ by a few ppm from the experimental ones, the shifts to lower frequency with increasing pucker angle are reproduced.

The chemical shifts of the ring carbons in the 1-methyl and 1-fluorobicyclo[*n*.1.1]alkane series **7a–c** and **8a–c**, respectively, were estimated by the procedures described previously and the results are compared with the experimental values in Table V. Again, even though the experimental and estimated results differ in several cases by a few ppm, the qualitative trends for the ring chemical shifts are followed and these are partially attributable to the effects of ring strain. Also entered in Table V are the estimated chemical shift values for the methyl carbons of each compound. These are the values for methylcyclobutane having the dihedral angles of these more strained compounds. Although there is a large (6.4 ppm) disparity for the bicyclo[3.1.1]heptane, the trend toward increased shielding with increasing strain is clear. In the 1-fluoro series there is a slight anomaly for the C1 carbon of **8b**, but it should be remembered that the IGLO results for this carbon gave the poorest correspondence with the experimental shifts in Table II. The estimated chemical shifts for the C2 and C3 carbons in Table V follow the experimental trends with increasing pucker angle.

VI. Conclusions

Calculated ^{13}C chemical shifts based on the IGLO method (HF/6-31G** geometries) for cyclobutane, substituted cyclobutanes, and the corresponding bicyclo[1.1.1]pentanes are in reasonable agreement with the experimental results. The largest disparities occur for CN carbons and the C1 carbons of the fluoro-substituted molecules. It seems likely that the agreement for these molecules will be improved by the use of larger basis sets for the geometry optimization and the shielding calculations. Although a number of ab initio MO calculations at this level of theory have been performed for some of these molecules, the results presented here provide a most comprehensive set over a range of pucker angles with a basis set of this quality.

For cyclobutane and the substituted cyclobutanes averaging of the chemical shifts over the puckering potential leads to values which differ from the equilibrium values by no more than 1 ppm. Values as small as these are consistent with opposite parities for the shielding curves and the puckering potentials for angles around the minimum energies. Even though the potential barriers for **1–4** are underestimated at this level of theory, it appears that this affects the pucker angle averages by no more than 0.2 ppm.

The calculated angular dependencies of ^{13}C chemical shifts in the cyclobutane series provide a good way of interpreting the ^{13}C chemical shifts of the carbons in highly strained four-membered rings. Predictions that the effects of increasing strain will be to shift all the ring carbons to higher frequency except for the C1 carbon of 1-fluoro-substituted compounds are confirmed by the experimental shifts for the 1-substituted bicyclo[1.1.1]pentanes. Conformational and substituent effects are analyzed in terms of the variations in the IGLO C–H and C–C bond paramagnetic contributions. The most important factor is the strong sensitivity to dihedral angle of the paramagnetic bond contributions for equatorial C–H or C–X bonds. The PBC's for *axial* C–H bonds vary by less than 1 ppm over a 40° dihedral angle range while those for the *equatorial* C–H bonds change by more than five times this much. An interesting parallel is found in the previous study of the PBC's for *n*-butane: for C1 chemical shifts near cis arrangements one of the most important PBC's is that for the C1–H bond pointing away from the C4 methyl group.[1] The paramagnetic bond contributions, which are implicit in distributed origins approaches, provide somewhat more detail than the chemical shifts but they do not specify the electronic origins for observed effects. However, the trends noted here toward more negative PBC's and decreasing bond lengths with increasing pucker angles suggest that increasing σ-bond orders may be important factors.[5]

The α-, β-, and γ-effects at the ring carbons due to –CN, $-CH_3$, and –F substituents were examined as a function of dihedral angle. There are substantial differences, not only among these results but with previous IGLO substituent effects for aliphatic compounds.[1,2] The only general observations that seem to be appropriate are that α-effects are *usually* positive (deshielding), β-effects are *almost always* positive, and γ-effects are *usually* negative (shielding). In contrast to the usual dogma in this area, steric compression is clearly not necessary for observing large γ-effects. Even though the conformational dependencies vary considerably with substituent, there are some similarities: for angles less than about 100° all of the curves show a monotonic increase in the magnitudes, but for angles greater than about 100°, most of these substituent effects are predicted to lead to increased shielding with increasing dihedral angle. Estimates were made of the ^{13}C shifts for the cyclobutane ring carbons of the 1-substituted bicyclo[*n*.1.1]alkanes by extrapolating the substituent effects to the larger pucker angles. The qualitative conformity of these estimates with the experimental data indicates that dominant factors are ring strain (as measured by the pucker angle) as well as the nature of the substituent. Thus, the ^{13}C chemical shifts are also promising conformational probes in *strained* cyclic and bicyclic molecules.

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Supplementary Material Available: Tables of all of the calculated shielding data and energies (5 pages). Ordering information is given on any current masthead page.