formation about the hydrogen bond length or hydrogen bond strength in the solid state.

Registry No. H-Gly-Gly-Val-OH, 20274-89-9; ClAc-Gly-Gly-OH, 15474-96-1; H-Pro-Gly-Gly-OH, 7561-25-3; H-Ala-Gly-Gly-OH, 3146-40-5; H-Gly-Gly-OH, 556-50-3; H-Gly-Phe-Gly-OH, 14656-09-8; H-Gly-DL-Thr-OH, 27174-15-8; H-Gly-Thr-OH, 7093-70-1; H-Val-Gly-Gly-OH, 21835-35-8; H-Sar-Gly-Gly-OH, 18479-98-6; H-Gly-Gly-OH·HNO_3, 50998-12-4; H-DL-Leu-Gly-Gly-OH, 4337-37-5; H-Gly-DL-Phe-OH, 721-66-4; H-Gly-Phe-OH·HCl, 78410-67-0; H-Gly-Phe-OH·TsOH, 40301-89-1; H-Gly-OH, 56-40-6; glycine homopolymer, 25718-94-9; polyglycine, SRU, 25734-27-4.

Low-Temperature ^{13}C Magnetic Resonance. 8. Chemical Shielding Anisotropy of Olefinic Carbons[1a]

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Abstract: The principal values of the ^{13}C NMR shielding tensor were measured at cryogenic temperatures for a series of olefinic carbons, including methyl-substituted ethylenes, 1-methyl- and 1,2-dimethylcycloalkenes, methylenecycloalkanes, and bicyclo[*n*.*m*.0]alkenes. Information on the orientation of the principal axes was obtained from ab initio calculations of the chemical shielding tensors using the IGLO (individual gauge for localized orbitals) method. The results for several compounds with unusual principal values of the shielding tensor were analyzed in terms of the bond contributions in the principal axis system.

Over the last several years the combination of low-temperature ^{13}C NMR spectroscopy with the quantum mechanical calculation of the chemical shielding tensor has been shown to be very valuable in the interpretation of chemical shielding data in small organic molecules.[2] Studies on carbon atoms in a wide range of bonding situations have been completed, including methyl groups,[3] methine carbons,[4] and methylene carbons.[5] Other studies have looked at carbons in linear molecules[6] and in the series cyclopropane, bicyclo[1.1.0]butane, and [1.1.1]propellane.[7] The calculations were used to determine the orientation of the principal axis system of the chemical shielding tensor in the molecular frame, information that is not determined experimentally from natural abundance powder samples.

Previously the experimental chemical shielding values for the cycloalkenes from cyclopropene to cyclooctene, ethylene, *cis*-2-butene, and *trans*-2-butene were reported.[8] For the sake of completeness these experimental results are also included here along with their calculated shielding tensors. A previous experiment on ethylene-*1,2*-$^{13}C_2$[9] provided the orientation of the principal axis system in the molecular frame. The findings were that the downfield component, σ_{11}, was perpendicular to the double bond and lay in the plane of the molecule, σ_{22} was along the double bond, and σ_{33} was perpendicular to the double bond and to the plane of the molecule. Similar orientations have been found in several single-crystal studies,[10,11] and in another dipolar study[12] on more complicated alkene derivatives. Early theoretical studies have also shown the same results for the orientation of the shielding tensors.[13-16]

In this paper, the experimental principal values of the shielding tensor as well as the calculated results are presented for a wide range of olefinic carbons. The types of olefinic carbons that are studied can be divided into five groups: methyl-substituted ethylenes, cycloalkenes, 1-methyl- and 1,2-dimethylcycloalkenes, methylenecycloalkanes, and bicyclo[*n*.*m*.0]alkenes. The structures of the compounds studied are shown in Figure 1.

Experimental and Computational Methods

Materials. Commercial samples of tetramethylethylene, methylenecyclobutane, methylenecyclopentane, propene, 1-methylcyclopentene, and isobutene were used without any further purification. A sample of 1,2-dimethylcyclobutene was provided by Professor D. Aue (University of California at Santa Barbara). The precursor for the synthesis of bicyclo[2.2.0]hex-1(4)-ene as well as a sample of bicyclo[3.2.0]hept-1(4)-ene was provided by Professor K. B. Wiberg (Yale University). Drs. P. J. Okarma and J. J. Caringi (Yale University) provided a sample of bicyclo[3.3.0]oct-1(5)-ene.

The remaining compounds were synthesized according to published literature procedures: methylenecyclopropane,[17] 1,2-bismethylenecyclobutane,[18] 1,2-dimethylcyclohexene,[19] bicyclo[3.2.0]hept-1(5)-ene,[20] bi-

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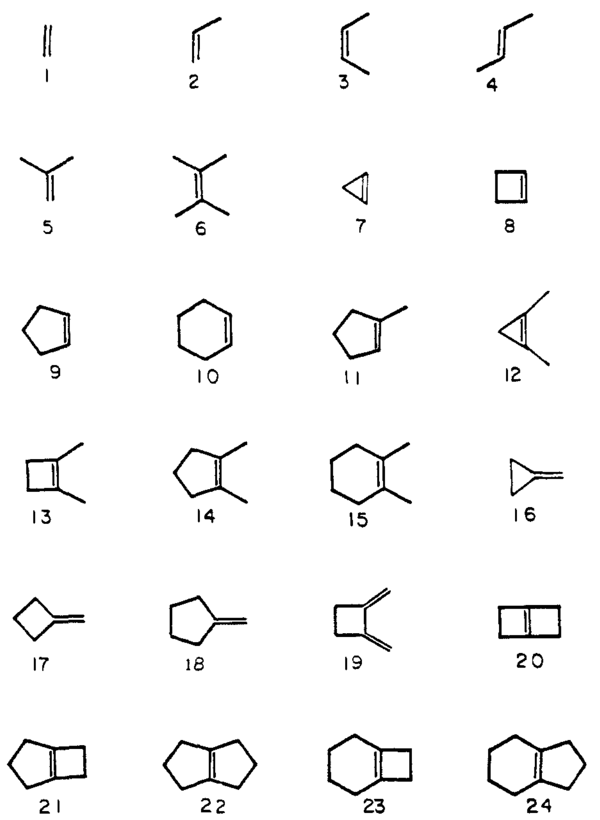

Figure 1. Structures of the olefins studied.

cyclo[4.2.0]oct-1(6)-ene,[20] bicyclo[4.3.0]non-1(6)-ene,[21] bicyclo[3.3.0]-oct-1(5)-ene,[22] and bicyclo[2.2.0]hex-1(4)-ene.[23] 1,2-Dimethylcyclopentene was prepared using the same procedure as 1,2-dimethylcyclohexene, starting with 2-methylcyclopentanone instead of 2-methylcyclohexanone.

In all cases except for bicyclo[2.2.0]hex-1(4)-ene, the compounds are completely stable at room temperature. Bicyclo[2.2.0]hex-1(4)-ene readily polymerizes at room temperature (the neat olefin has a half-life of less than 10 s at −23 °C)[24] and therefore had to be trapped on the cold tip immediately after generation. This compound was generated by the thermolysis of the tosylhydrazone of [2.3]spirohexan-4-one at 190 °C and trapping of the products on the cold tip of the cryostat.[23] The products of this thermolysis were shown by solution NMR to be a mixture of 1,2-bismethylenecyclobutane (**19**) and bicyclo[2.2.0]hex-1(4)-ene (**20**), in an approximately 1:4 ratio. The exact ratio is a function of the pressure in the system during the reaction, indicating that **19** is formed from **20** during the reaction.[23] The above procedure was followed using the cryostat's cold tip as the trapping surface. The distance between the hot surface and the cold tip was kept to a minimum (approximately 4 in.) to minimize the chances of rearrangement, and the rate of thermolysis was kept slow enough that the temperature at the cold tip did not increase more than a few degrees. After the thermolysis was complete, the system was sealed off between the thermolysis vessel and the cold tip. In one case the spectrum obtained appeared not to have any appreciable amount of the side product **19** present; it is from this spectrum that the principal values of the shielding tensor were obtained.

Measurements. The cryogenic equipment and the home-built spectrometer used have been previously described.[8] All spectra were recorded on neat samples at a temperature of approximately 20 K, using a standard cross-polarization pulse sequence[25] with contact times of 3 ms and recycle times of 3 to 5 s.

Experimental shieldings were referenced to an external sample of $(CH_3)_4Si$. The experimental spectra were analyzed either by direct simulation and comparison to the experiment or by the use of a SIMPLEX fitting routine.[26] In every case except ethylene, the σ_{33} component of the olefinic shielding tensor was concealed by the aliphatic carbon signals. In most of these cases the value for this component had to be estimated from the liquid shift value and the other two components. The estimated error in the reported shielding values is 2–3 ppm; however, for the components that were not measured directly, it may be even larger since we cannot provide an accurate estimate of the change in the isotropic chemical shift on going from solution to the solid state in these compounds.

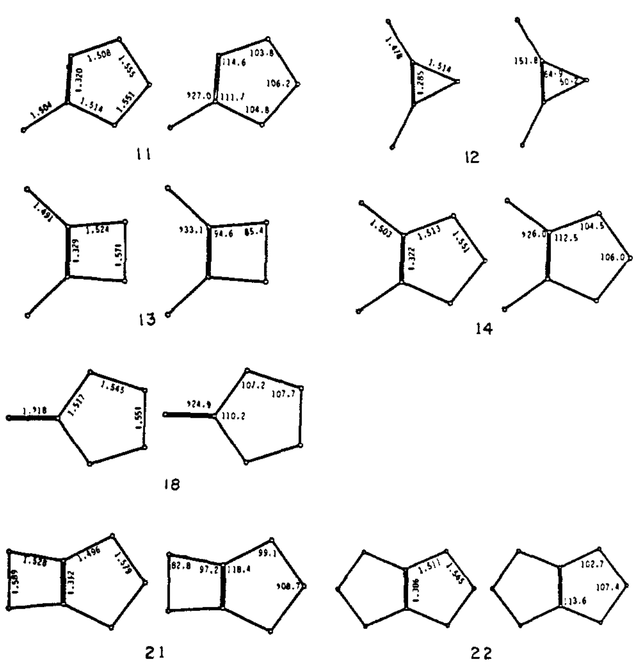

Figure 2. Optimized C–C bond lengths (in Å) and C–C–C bond angles (in deg) for 1-methylcyclopentene (**11**), 1,2-dimethylcyclopropene (**12**), 1,2-dimethylcyclobutene (**13**), 1,2-dimethylcyclopentene (**14**), methylenecyclopentane (**18**), bicyclo[3.2.0]hept-1(5)-ene, (**21**), and bicyclo-[3.3.0]oct-1(5)-ene (**22**).

Calculations. The calculation of the chemical shielding tensors was done using the IGLO (individual gauge for localized orbitals) method [27-30] using Huzinaga[31] Gaussian basis sets. Basis set I was of double-zeta (ζ) quality [carbon, (7,3) contracted (4111,21), and hydrogen, (3) contracted (21)]. Calculations at this basis set level were done on molecules with seven or fewer carbon atoms. For molecules with four or fewer carbon atoms, calculations were also performed using basis set II, a larger basis set that included polarization functions [carbon, (9,5,1) contracted (51111,311,1), d orbital exponent of 1.0, and hydrogen, (5,1) contracted (311,1), p orbital exponent of 0.7]. The calculated principal values of the shielding tensor were converted to the $(CH_3)_4Si$ scale as described previously.[5]

Experimental geometries were used whenever available: ethylene,[32] propene,[33] *cis*-2-butene,[34] *trans*-2-butene,[35] isobutene,[36] tetramethylethylene,[37] cyclopropene,[32] cyclobutene,[38] cyclopentene,[39] cyclohexene,[40] methylenecyclopropane,[41] methylenecyclobutane,[42] and 1,2-bis-

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Table I. Experimental and Calculated Principal Values of Olefinic ^{13}C Shielding Tensors[a]

	compound	σ_{11}		σ_{22}		σ_{33}		σ_{av}		
		exptl	calcd	exptl	calcd	exptl	calcd	exptl	calcd	liq
1	ethylene[b]	234	278	120	114	24	−1	126	130	123.3
			273		113		13		133	
2a	propene C_1	226	272	97	97	[17]	15		128	113.4
			253		90		27		123	
2b	propene C_2	253	288	133	125	[12]	0		138	132.7
			283		131		17		144	
3	*cis*-2-butene[b]	232	294	119	126	22	14	124	145	124.6
			280		125		30		145	
4	*trans*-2-butene[b]	232	273	113	112	37	24	127	136	126.0
			261		111		42		138	
5a	isobutylene C_1	217	259	86	86	[29]	29		125	110.7
			233		75		39		116	
5b	isobutylene C_2	268	284	152	134	[5]	−2		139	141.7
			288		145		14		149	
6	tetramethylethylene	222	254	119	118	29	11	123	128	122.8
7	cyclopropene[b]	239	293	79	83	5	−3	108	124	108.7
			281		79		−2		119	
8	cyclobutene[b]	244	291	138	143	[30]	26		153	137.2
			278		139		33		150	
9	cyclopentene[b]	235	281	118	115	39	29	131	142	130.8
10	cyclohexene[b]	236	266	123	122	[23]	4		131	127.4
11a	1-methylcyclopentene C_1	220	259	102	96	[51]	31		129	124.2
11b	1-methylcyclopentene C_2	244	270	128	115	[48]	24		136	140.1
12	1,2-dimethylcyclopropene		281		72		1		118	
13	1,2-dimethylcyclobutene	235	274	131	122	[45]	27		141	137.0
14	1,2-dimethylcyclopentene	230	261	119	104	[46]	28		131	131.5
15	1,2-dimethylcyclohexene	214		117		[46]				125.6
16a	methylenecyclopropane C_1	200	228	97	101	[12]	4		111	103.0
			218		96		18		111	
16b	methylenecyclopropane C_2	220	236	185	176	[−13]	−26		129	130.7
			245		189		−22		137	
17a	methylenecyclobutane C_1	208	239	90	99	[17]	3		114	105.1
17b	methylenecyclobutane C_2	253	262	154	143	[44]	18		141	150.2
18a	methylenecyclopentane C_1	220	246	82	83	[13]	12		114	104.9
18b	methylenecyclopentane C_2	262	279	145	132	[52]	40		150	153.0
19a	1,2-bismethylenecyclobutane C_1	204	254	95	100	[10]	9		121	103.1
19b	1,2-bismethylenecyclobutane C_2	250	282	144	139	[55]	40		154	149.7
20	bicyclo[2.2.0]hex-1(4)-ene	323	363	128	116	[46]	36		172	165.8
21	bicyclo[3.2.0]hept-1(5)-ene	271	313	123	111	[56]	41		155	150.1
22	bicyclo[3.3.0]oct-1(5)-ene	244	265	118	96	[76]	53		138	146.0
23	bicyclo[4.2.0]oct-1(6)-ene	253		130		[43]				142.1
24	bicyclo[4.3.0]non-1(6)-ene	235		128		[41]				134.5

[a] Experimental values referenced to Me_4Si, calculated values to CH_4. σ_{33} values in brackets were determined by combining the σ_{11} and σ_{22} values measured with the isotropic shift measured in solution. For all molecules with two sets of calculated results the first line is for basis set I and the second for basis set II, as described in the text. For all molecules with two olefinic carbons, the first one listed is the less substituted carbon. [b] Experimental values from: Zilm, K. W.; Conlin, R. T.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1980**, *102*, 6672.

methylenecyclobutane.[43] For bicyclo[2.2.0]hex-1(4)-ene[44] a 4-31G optimized geometry was used. Geometry optimizations on 1-methylcyclopentene, 1,2-dimethylcyclopropene, 1,2-dimethylcyclobutene, 1,2-dimethylcyclopentene, methylenecyclopentane, and bicyclo[3.2.0]hept-1-(5)-ene were completed at the 4-31G basis set level using the GAUSSIAN 80[45] or GAUSSIAN 82[46] packages. For bicyclo[3.3.0]oct-1(5)-ene the geometry optimization was done at the STO-3G basis set level. The optimized heavy atom bond lengths and angles are shown in Figure 2.[47] Among the geometries optimized 1,2-dimethylcyclopentene was the only molecule with a nonplanar skeleton, with C-3 of the ring found to be 4° out of the plane of the molecule. The calculated bond lengths and angles are very similar to those obtained by Wiberg and co-workers for other small strained alkene rings including bicyclo[2.2.0]hex-1(4)-ene.[44,48]

Results and Discussion

The measured and the calculated principal values of the shielding tensor for the olefinic carbons are reported in Table I. For all molecules with two distinct olefinic carbons C_1 is always the less substituted carbon. In the cases where the calculations

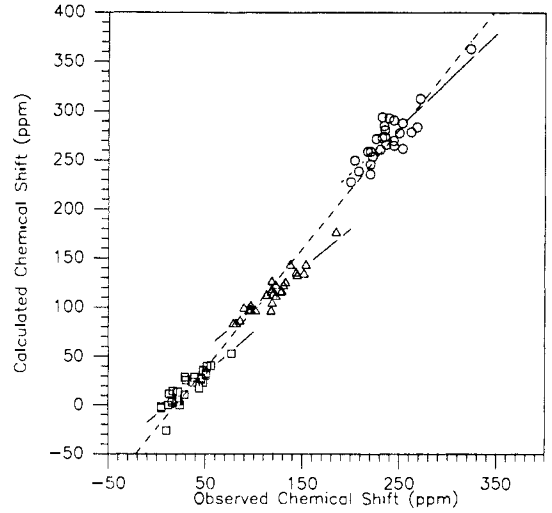

Figure 3. Correlation between experimental and calculated principal values at the double-ζ basis set level. Circles are σ_{11}, triangles σ_{22}, and squares σ_{33}. Solid lines are least-square fits on the individual components, the dashed line on all data.

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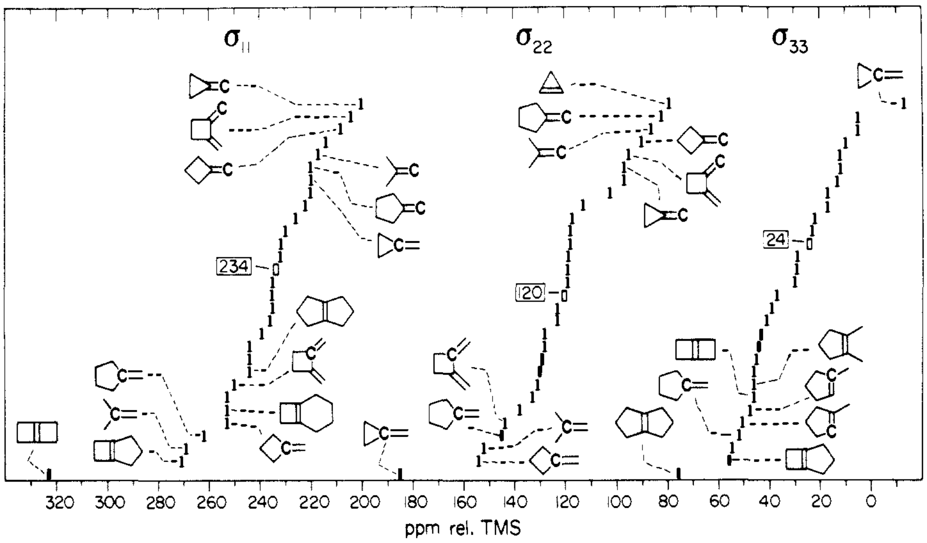

Figure 4. Plots of rank order of experimental principal values of the shielding tensors for all olefinic carbons studied. The values for ethylene are indicated by open marks. Shift values discussed in text are labeled with the chemical structure.

were done with two different basis sets, the first line gives the results obtained with basis set I and the second those with basis set II.

The correlation between the experimental principal values and those calculated with basis set I is shown in Figure 3. The least-squares fit has a slope of 1.22 ± 0.02 and an intercept of -24 ppm, with a correlation coefficient of 0.9920. The results of the least-squares fit on each of the components are as follows: σ_{11} slope of 0.94 ± 0.10, intercept 48 ppm, and correlation coefficient of 0.8776; σ_{22} slope of 0.82 ± 0.12, intercept 17 ppm, and correlation coefficient of 0.9492; σ_{33} slope of 0.85 ± 0.18, intercept -10 ppm, and correlation coefficient of 0.8900. With basis set I the overall agreement between the experimental and theoretical chemical shielding tensor components is not quite as good as in previous studies on aliphatic carbons,[3-5] especially for the σ_{11} values. In all cases the σ_{11} component is calculated to be from 9 to 62 ppm further downfield than experimental results. In most cases the calculated value of σ_{22} is quite close to the experimentally determined one, whereas σ_{33} is sometimes calculated to be too far upfield. The agreement between the experimental and calculated isotropic chemical shifts is quite good, with only a few cases in which the difference is over 5 ppm; in these cases almost all of the error in σ_{iso} can be traced to σ_{11}. The agreement between experimental and calculated isotropic values is therefore often a consequence of a cancellation of the errors in σ_{11} and σ_{33}. While the larger basis set which includes polarization functions generally improves the agreement for the individual components, the degree of improvement is disappointingly small, especially for σ_{11}. With the larger basis set the calculated value of σ_{33} generally improves, but because of the inadequacies in σ_{11} the agreement between the isotropic chemical shift and the calculated average deteriorates.

In the case of ethylene an IGLO calculation was also done with a third basis set to find out whether better agreement between the experimental and calculated σ_{11} could be obtained. The third basis set was (11,7,2/7,2) contracted to (5111111,211111,11/211111,11) with carbon d exponents of 0.5 and 2.0 and hydrogen p exponents of 0.5 and 1.0; the calculated principal values were 276, 112, and 16 ppm. The fact that these results are nearly the same as those calculated with basis set II indicates that further enlargement of the basis set has a negligible effect. Holler and Lischka[49] have also reported a calculation on ethylene using the coupled Hartree–Fock method. In their calculation with a (10,6,2/4,1) basis set, the calculated principal values were 277, 112, and 18 ppm with respect to CH_4. Again, the IGLO and CHF results are nearly the same, illustrating the fact that the IGLO theory and the CHF theory converge for large basis sets.[27] Therefore, the inability of the calculations to reproduce the experimentally observed values does not seem to be a problem of the quality of the basis set used; instead it is a clear indication of the need for the inclusion of correlation effects in the calculation of the ^{13}C shielding tensor for multiply bonded carbons. A similar conclusion has been recently reached in the study of ^{15}N shielding tensors for compounds containing N=N bonds.[50]

For each component, the majority of both the experimental and calculated values fall within a relatively narrow range, as shown in Figure 4. Unfortunately, the ordering of the compounds within each group is not monotonic between the experimentally determined and the calculated values. This prevents a refined parameterization of the shielding components for an olefinic carbon in typical bonding situations. However, the olefinic components which do not fall in the middle range of each group, (i.e., carbons which have one or more distinctive components) generally fall sufficiently outside of this middle range that the experimental and the calculated data correlate better, thus allowing an analysis of the effects leading to unusual shielding components. The structures of the compounds with atypical olefinic carbons are also indicated on Figure 4. It is obvious that the group of molecules with one or more unusual component is identical with the group of molecules which have atypical isotropic chemical shifts. No cases were found in which the unusual components cancel each other to give a typical isotropic value. For the σ_{33} component, all the compounds which have a five-membered ring with a sp^2 carbon are shifted downfield with respect to σ_{33} of ethylene; this trend is also observed in the calculated results.

Orientation of the Principal Axis System. Along with the principal values of the chemical shielding tensor the calculations also provide the principal axis system (PAS) or the orientation of the principal shielding directions in the molecular frame. While molecular symmetry can be helpful in determining the direction of one or more of the principal axes, information about which component is located along each of these directions is provided by theory or analogy to ethylene. The complete shielding tensor cannot be obtained from powder patterns on natural abundance samples unless there is at least a C_3 symmetry axis through the carbon of interest. In general the complete shielding tensor can only be experimentally determined by studies on single crystals or on doubly labeled materials.[25] As neither of these techniques is readily applicable to the large group of molecules in this study, the information on the orientation of the principal axis system in the molecular frame depended upon the calculations. This method has been used in the past on several series of molecules with good results.[3-5,7] In the case of olefinic carbons the difference between the individual components is large enough that there are

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(49) Holler, R.; Lischka, H. *Mol. Phys.* **1980**, *41*, 1017.

(50) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 5950.

Table II. Angle of Rotation of In-plane Components of the Olefinic Shielding Tensor from the Principal Axis System Defined by Ethylene

compound		angle[a]
2a	propene C_1	0.0, 0.4
2b	propene C_2	2.6, 3.3
3	*cis*-2-butene	2.2, 3.4
4	*trans*-2-butene	4.7, 5.7
7	cyclopropene	18.4, 20.5
8	cyclobutene	1.0, 2.6
11a	1-methylcyclopentene C_1	−0.5
11b	1-methylcyclopentene C_2	−0.4
12	1,2-dimethylcyclopropene	15.4
13	1,2-dimethylcyclobutene	1.8
19a	1,2-bismethylenecyclobutane C_1	1.8
19b	1,2-bismethylenecyclobutane C_2	0.1
21	bicyclo[3.2.0]hept-1(5)-ene	−2.2

[a] The angle, in degrees, that the σ_{22} direction makes with the double bond. Positive angles indicate the direction of rotation is toward the larger of the two substituents on the carbon of interest. The first angle is from calculations with basis set I; the second from calculations with basis set II.

no difficulties in associating the calculated components with the experimental components.

Several of the compounds have D_{2h} or C_{2v} symmetry, and therefore their principal axes are restricted to the same directions as in ethylene: **5**, **6**, **16**, **18**, **20**, and **22**. In all cases the calculated orientation was identical with that described earlier for ethylene,[9] with σ_{33} perpendicular to the plane of the molecule, σ_{22} along the double bond, and σ_{11} perpendicular to the double bond and in the plane of the molecule.

In some of the compounds only one of the two planes of symmetry that contain the olefinic carbons found in ethylene is retained, namely the plane containing all of the heavy atoms. This is the situation in the planar compounds **2**, **3**, **4**, **7**, **8**, **11**, **12**, **13**, **19**, and **21**. The σ_{33} component is always the component determined to be perpendicular to this plane. The remaining two components are free to be in any orientation in this plane. Except for the cyclopropenes, **7** and **12**, σ_{22} is always calculated to be nearly along the double bond and σ_{11} nearly perpendicular to the double bond. The calculated angles of deviation from the ethylene-like orientation are given in Table II. A positive angle is an indication of rotation toward the substituent or toward the bulkier of the two substituents. The first number is the angle calculated with the basis set I and the second with basis set II when used. In all cases where calculations were done with more that one basis set the orientations agree to within 2.1°.

In **17** only the plane that contains the π bond is retained from ethylene. This requires the direction perpendicular to this plane to be a principal direction; the calculation places σ_{11} along this axis in both of the carbons. For C_1 σ_{22} is found to deviate by 0.5° from the double bond direction, and in C_2 the angle of deviation from the bond is 2.1°. In C_1 the sense of rotation is the same as the sense of the deviation from planarity of the molecule, but for C_2 the sense of the rotation is the opposite.

The final group of compounds is that in which there exist none of the symmetry planes found in ethylene. This group includes **9**, **10**, and **14**. In these cases it is most convenient to describe the orientation of the principal axis system by the direction cosines between the principal axes of the shielding tensor and the symmetry axes in ethylene. This information is provided in Table III. It is seen once again that the principal axes are oriented essentially the same way as in ethylene (the largest angular deviation is only 4.2°).

It is evident from the results of the IGLO calculations that the orientation of the principal axis system for olefinic carbons is fairly insensitive to the substituents or the bonding situation of the carbon. In order to get a large deviation in the orientation, the substituents must place a significant amount of strain at the double bond, as is the case in cyclopropene where the calculated orientation deviates by an angle of 18.4° with basis set I and 20.5° with the basis set II, and in 1,2-dimethylcyclopropene where the angle is 15.4° (basis set I). Otherwise the principal axis system always differs by less than 5° from the orientation found in ethylene. Thus, the calculations strongly suggest that the orientation of the shielding tensors is dominated by the local symmetry of the π electrons. This result is in general agreement with a single-crystal study on dihydromuconic acid which determined that σ_{11} was perpendicular to the double bond and 6 ± 3° above the nodal plane, σ_{22} is along the bond and 7 ± 3° below the nodal plane of the double bond, and σ_{33} is 79 ± 3° from the nodal plane of the double bond;[10] this result indicates that not even the presence of large bulky substituents disturbs the effect of the local symmetry. The results of single-crystal studies on dimethylmaleic anhydride and acrylamide[11] as well as a dipolar study on *trans*-polyacetylene[12] also indicate the dominance of the local symmetry of the site in the determination of the orientation of the olefinic shielding tensor.

Table III. Direction Cosines between the Principal Axis System of the Shielding Tensor of the Olefinic Carbon and the Principal Axis System Defined by Ethylene

compound			direction cosine matrix[a]		
			A	*B*	*C*
9	cyclopentene	α	0.99961	0.02737	−0.00636
		β	−0.02763	0.99860	−0.04509
		γ	0.00512	0.04525	0.99896
10	cyclohexene	α	0.99999	−0.00263	−0.00380
		β	0.00235	0.99734	−0.07289
		γ	0.00398	0.07288	0.99733
14	1,2-dimethylcyclopentene	α	0.99918	−0.03934	0.00938
		β	0.03942	0.99919	−0.00761
		γ	−0.00907	0.00797	0.99993

[a] *A*, *B*, and *C* denote the axis system in ethylene, and α, β, and γ the axis system in the compound of interest.

Principal Values of Shielding Tensor. As stated earlier, for the majority of the olefinic carbons there is nothing unusual about any of the principal values in comparison with those for ethylene. This is true for both the experimental and the calculated values. These ordinary olefinic carbons include all of the cycloalkenes except cyclopropene, the methylated cycloalkenes, the methylated alkenes except for isobutylene, and the bicycloalkenes with six-membered rings. The olefinic carbons with unusual shielding components are found in the methylenecycloalkanes, isobutylene, cyclopropene, and the bicyclo[*n*.*m*.0]alkenes with *n* or *m* <5.

A convenient and useful method of analysis of the results of the IGLO calculations is to compare the bond contributions, either in the principal axis system of the shielding tensor or in the local bond frame.[51] Only the paramagnetic terms need be considered, as the diamagnetic portion of the shielding is invariant to the changes in the bonding environment for olefinic carbon shielding tensors.[51] The following comparisons are made in the symmetry frame of ethylene; this is essentially the same as the principal axis system since the deviations from the orientation found in ethylene are minor for the compounds discussed below. Normally, at least 90% of the paramagnetic portion of the shielding tensor can be recovered by considering the paramagnetic contribution of the directly attached bonds. Among the olefinic carbons, this was found to be the case for the contribution of these bonds toward σ_{11} and σ_{22}; for σ_{33} this contribution was 80 to 90%. The only significant exceptions were σ_{22} and σ_{33} of both cyclopropene and 1,2-dimethylcyclopropene. In the case of the cyclopropene compounds the increased importance of the remote bonds to the paramagnetic shielding is probably due to problems in the description of the localized bonds leading to a more delocalized description of the electronic structure. This effect probably also plays a role in the large deviation seen in the orientation of the principal axis system as well as in the presence of large antisymmetric components.[52,53]

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(51) Facelli, J. C.; Grant, D. M.; Michl, J. *Int. J. Quantum Chem.* **1987**, *31*, 45.

(52) Facelli, J. C.; Orendt, A. M.; Grant, D. M.; Michl, J. *Chem. Phys. Lett.* **1984**, *112*, 147.

Table IV. Paramagnetic Bond Contributions[a] to the Shielding in the Olefinic Carbons in Ethylene and the Methylenecycloalkanes

compound		C_1[b]				C_2[b]			
		bond	σ_{11}	σ_{22}	σ_{33}	bond	σ_{11}	σ_{22}	σ_{33}
1	ethylene	σ_p(C=C)	-231	-9	-18				
		σ_p(C—H)	-63	-146	-6				
5	isobutylene	σ_p(C=C)	-220	-4	-26	σ_p(C=C)	-234	-4	-17
		σ_p(C—H)	-56	-128	-20	σ_p(C—C)	-72	-166	-3
16	methylenecyclopropane	σ_p(C=C)	-193	-11	-21	σ_p(C=C)	-188	-32	-9
		σ_p(C—H)	-50	-135	-6	σ_p(C—C)	-67	-194	13
17	methylenecyclobutane	σ_p(C=C)	-202	-13	-23	σ_p(C=C)	-208	-16	-29
		σ_p(C—H)	-52	-122	-11	σ_p(C—C)	-70	-171	-8
18	methylenecyclopentane	σ_p(C=C)	-211	-5	-23	σ_p(C=C)	-208	-4	-26
		σ_p(C—H)	-53	-125	-10	σ_p(C—C)	-70	-170	-28
19	1,2-bismethylenecyclobutane[c]	σ_p(C=C)	-214	-10	-19	σ_p(C=C)	-222	-21	-32
		σ_p(C—H)	-30	-62	-6	σ_p(C—C)	-40	-77	-13
		σ_p(C—H′)	-27	-70	-6	σ_p(C—C′)	-33	-82	-10

[a] Bond contributions are in the principal axis system of ethylene. All values are absolute paramagnetic shielding contributions. For the C—C bond the listed value is the sum for both obes of the olefinic bond, and for the C—H and C—C bonds the value is the sum from both attached groups. [b] C_1 is the external olefinic carbon and C_2 the ring olefinic carbon of the methylenecycloalkanes. [c] In **19** C–H is the bond with the H toward the 1,4 C–C bond, C–H′ represents the H toward the second methylene group, C–C is the 1,2 carbon bond, and C–C′ the 1,4 carbon bond.

Among all of the methylenecycloalkanes and including isobutylene, there is a large difference between the isotropic chemical shifts of the two olefinic carbons. The isotropic chemical shift of the unsubstituted olefinic carbon, C_1, is shifted from 8 to 26 ppm upfield from ethylene while that of the substituted carbon, C_2, is shifted from 19 to 34 ppm downfield. The one exception to this is the C_2 of methylenecyclopropane whose isotropic chemical shift is only 7 ppm downfield from that of ethylene; this could possibly be due to the additional effect of strain in the three-membered ring. Among the remaining carbons in this series the unusual downfield shift of σ_{iso} for C_2 is seen to be due to changes in σ_{11} and σ_{22}. Both components are found much further downfield than the corresponding components in ethylene, and as the ring size is increased from three to five the values of both σ_{11} and σ_{22} approach those observed in isobutylene; there is no trend observed in the changes in σ_{33}. For C_1 a large upfield shift in both σ_{11} and σ_{22} is observed, with the majority of the change found in σ_{22}. Once again no clear trend is observed in the variations of σ_{33}.

In Table IV the paramagnetic bond contributions of the directly attached bonds are listed for ethylene, isobutylene, and several methylenecycloalkanes. All contributions are from the calculations done with basis set I. The values listed are absolute paramagnetic shieldings and are in the principal axis system of ethylene. This analysis indicates that for σ_{22} the difference between the two olefinic carbons of a given compound is nearly completely due to the differences in the contributions of the C–H bonds on C_1 and the C–C bonds on C_2. For C_1 the mixing of the C–H bonds with the antibonding orbitals of the olefinic bond causes an upfield shift with respect to the same contribution in ethylene, whereas for C_2 the C–C bonds produce a downfield shift. The variations in the contributions from the double bond do not significantly contribute to the difference seen in σ_{iso}, except in methylenecyclopropane and 1,2-bismethylenecyclobutane, where the differences are 21 and 11 ppm, respectively. In methylenecyclopropane this difference could possibly be related to the strain of the cyclopropane ring. In the σ_{11} component the differences can be traced to contributions due to both the C=C bond and the substituent bonds, with both effects having nearly equivalent weighting. Again the contributions to the shielding at C_1 produce an upfield shift while the contributions at C_2 produce a downfield shift from the values obtained in ethylene. The C_2 carbon of methylenecyclopropane is an exception with its σ_{11} component found upfield from that of ethylene, explaining why the σ_{iso} of this carbon is not shifted as far downfield as the remaining substituted carbons in this group.

In the bicyclo[*n*.*m*.0]alkenes the isotropic chemical shifts are found downfield from ethylene, with the larger shift seen in the compounds with the smaller rings, or the more highly strained systems. Bicyclo[2.2.0]hex-1(4)-ene has the most downfield isotropic shift known for an olefinic carbon in a hydrocarbon. The spectra of both bicyclo[2.2.0]hex-1(4)-ene and 1,2-bismethylenecyclobutane, the side product in the thermolysis used to generate **20**, are shown in Figure 5. While the quality of the spectrum of **20** is not as high as that of **19**, it is good enough to obtain the principal values listed in Table I with reasonable confidence. The quality of the fit in both cases can be seen from the spectral simulations included in Figure 5. The downfield shift in σ_{iso} is found to be due to downfield shifts in σ_{11} and σ_{33}; σ_{22} is relatively normal. The downfield shift in σ_{11} is the largest with σ_{11} of bicyclo[2.2.0]hex-1(4)-ene at 323 ppm and approaches the value of ethylene as the ring size increases. There is no clear trend in the value of σ_{33}; this could be due in part to the inadequacies in the measurement of this component.

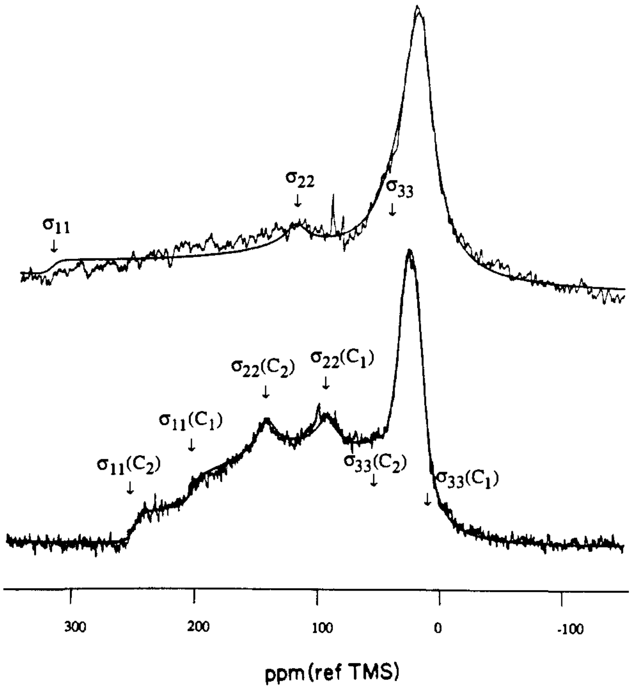

Figure 5. (Top) Experimental spectrum of bicyclo[2.2.0]hex-1(4)-ene (**20**) along with the best Simplex simulation. (Bottom) Experimental spectrum of 1,2-bismethylenecyclobutane (**19**), the side product in the formation of **20** along with the best Simplex simulation. Arrows indicate the position of the chemical shielding tensor components of the olefinic carbons.

Once again the shielding can be studied in terms of the attached bonds, and a comparison to ethylene or tetramethylethylene can be made. In Table V the paramagnetic bond contributions are listed for the attached bonds in these compounds. For this series the major variation in σ_{11} is found to be in the contribution of

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(53) Robert, J. B.; Wisenfeld, L. *Phys. Rep.* **1982**, *86*, 363.

Table V. Paramagnetic Bond Contributions[a] to the Shielding in Olefinic Carbons in Ethylene, Tetramethylethylene, and the Bicyclo[*n*.*m*.0]alkenes

compound		bond	σ_{11}	σ_{22}	σ_{33}
1	ethylene	$\sigma_p(\mathrm{C{=}C})$	−231	−9	−18
		$\sigma_p(\mathrm{C{-}H})$	−63	−146	−6
6	tetramethylethylene	$\sigma_p(\mathrm{C{=}C})$	−213	−5	−19
		$\sigma_p(\mathrm{C{-}C})$	−61	−153	−8
20	bicyclo[2.2.0]hex-1(4)-ene	$\sigma_p(\mathrm{C{=}C})$	−318	9	−17
		$\sigma_p(\mathrm{C{-}C})$	−71	−152	−8
21	bicyclo[3.2.0]hept-1(5)-ene[b]	$\sigma_p(\mathrm{C{=}C})$	−271	6	−25
		$\sigma_p(\mathrm{C{-}C})$	−19	−88	−7
		$\sigma_p(\mathrm{C{-}C'})$	−50	−62	−23
22	bicyclo[3.3.0]oct-1(5)-ene	$\sigma_p(\mathrm{C{=}C})$	−324	10	−23
		$\sigma_p(\mathrm{C{-}C})$	−62	−147	−35

[a] Bond contributions are in the principal axis system of ethylene. All values are absolute paramagnetic shielding contributions. For the C=C bond the listed values are for both lobes of the olefinic bond, and for the C—C bond the listed values are the sums of the two attached substituents except as indicated for **21**. [b] C–C is the contribution from the bond in the four-membered ring and C–C′ is the contribution from the bond of the five-membered ring. The sum of these two values should be used in comparison to the σ_p(C–C) given for the other compounds.

the C=C bond, with a small contribution to the downfield shift from the C—C bonds. As the ring size increases, the contributions from all of the bonds approach those found in both tetramethylethylene and ethylene in the same manner observed for σ_{iso}. The unusually large downfield shifts observed in σ_{33} can be traced mainly to the paramagnetic contributions of the C–C bonds; in this case the compounds with larger rings are shifted further downfield. An unusual but relatively modest effect is seen in upfield movement in the contribution of the C=C bond to σ_{22}. The variation between the C–C contributions for the several members of this series is also modest when the two different C–C contributions in **21** are summed and compared with the composite value for both C–C bonds in the other members of the series.

Conclusions

The chemical shielding data for olefinic carbons in a wide range of bonding situations have been presented. The values of the individual tensor components as well as the isotropic chemical shift have a wide range, but IGLO calculations suggest that the orientation of the principal axis system is relatively insensitive to the structural variations. The IGLO calculations had the greatest difficulty in reproducing the experimental principal values for σ_{11}. This difficulty was shown not to be due to the quality of basis set but indicates that it is necessary to include correlation effects in the calculation when dealing with multiply bonded carbon atoms.

A few generalizations can be made about the principal values of the chemical shielding tensor. For all olefinic carbons with an ethylene-like isotropic chemical shift, the principal values are not very different from those of ethylene. Compounds with unusual isotropic shifts in comparison to ethylene do have one or more distinctly different components. This was the case for two subgroups of the olefins, the methylenecycloalkanes and the bicyclo[*n*.*m*.0]alkenes. For the methylenecycloalkenes the unusual isotropic chemical shift was found to be due to unusual values of σ_{11} and σ_{22}, and in the bicyclo[*n*.*m*.0]alkenes to unusual values of σ_{11} and σ_{33}. As the ring size increases, in both groups the principal values as well as the isotropic chemical shift approach the values of ethylene. In both cases the differences can be almost entirely attributed to the contribution the directly attached bonds make to the paramagnetic shielding. Among the methylenecycloalkanes the unusual principal values of the shielding tensor can be traced to variations in the paramagnetic bond contribution of the C—H or C—C bond to σ_{22} and to the changes in the contributions of both the C=C bond and the C—H or C—C substituent bonds to σ_{11}. For the bicyclo[*n*.*m*.0]cycloalkenes the downfield shift in σ_{11} is nearly entirely seen in the contribution of the C=C bond while the shift in σ_{33} is due to the contribution of the C—C substituent bonds.

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Registry No. **1**, 74-85-1; **2**, 115-07-1; **3**, 590-18-1; **4**, 624-64-6; **5**, 115-11-7; **6**, 563-79-1; **7**, 2781-85-3; **8**, 822-35-5; **9**, 142-29-0; **10**, 110-83-8; **11**, 693-89-0; **12**, 14309-32-1; **13**, 1501-58-2; **14**, 765-47-9; **15**, 1674-10-8; **16**, 6142-73-0; **17**, 1120-56-5; **18**, 1528-30-9; **19**, 14296-80-1; **20**, 30830-20-7; **21**, 10563-10-7; **22**, 6491-93-6; **23**, 10563-11-8; **24**, 695-90-9.