

Low-Temperature Carbon-13 Magnetic Resonance of Solids.

1. Alkenes and Cycloalkenes

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Abstract: The ^{13}C shift tensors for a large variety of olefins including some of the cyclic variety are reported at 20 K. On the basis of existing studies and symmetry arguments the orientation of the tensor elements can in general be assigned to specific molecular axes for the olefinic carbons. With this information conclusions are then drawn, relating trends in the various tensor elements to geometric and electronic effects. The method shows great promise in elucidation of the geometrical origins of chemical shifts. Often the range of shifts encompassed by any individual tensor element is 3 times greater than that of the isotropic shifts in the series. Also described is the apparatus for obtaining ^{13}C cross-polarization spectra at cryogenic temperatures.

I. Introduction

The development of cross-polarization (CP)¹ spectroscopy is now beginning to yield a wealth of ^{13}C chemical shift tensors.^{2,3} The availability of such tensorial data from solids is expected to prove even more enlightening than that of isotropic data obtained on liquids as up to three times as much shielding information may be obtained. However, most of the data collected to date have been obtained at ordinary temperatures and only a few molecules small enough for accurate theoretical treatment have been run.^{4,5} Many small molecules are still gases or liquids or are unstable at typical operating temperatures. Conspicuously absent from the current literature are the shift tensors for small olefins and aliphatics because of their very low melting points.

At cryogenic temperatures the problem of obtaining solid samples is solved. Furthermore the sensitivity of the NMR experiments is greatly enhanced over that at room temperature due to the larger Boltzmann factor.⁶ This increase is enough to make possible observation of shift tensors or even dipolar spectra of molecules isolated at 1% concentration in low-temperature argon matrices.^{7,8} Matrix isolation also extends the technique to the characterization of species so reactive as to be present only when trapped in such inert environments.

The usefulness of these low-temperature techniques is illustrated in this study of a series of small olefins including some of the cyclic variety. Trends in the tensor components are discussed and compared with the isotropic⁹ shifts. The nature and extent of substitution and important three-dimensional structural features are related to the tensorial shift values.

II. Experimental Section

A. Apparatus. An apparatus for ^{13}C CP measurements down to 20 K has been built in this laboratory which uses a closed-cycle helium refrigeration unit for cooling. A schematic of the apparatus is shown in Figure 1. This method of cooling is advantageous in that cryogenic liquids are not used thereby making time averaging over long periods economically possible. It is well-known that the presence of He gas in the probe can cause arcing, especially at the high power levels typically used in CP experiments.¹⁰ This problem is avoided in our system as no

liquid He is used in the probe to achieve cryogenic temperatures.

The refrigeration unit is an Air Products Model 202-B close-cycle helium refrigeration unit with a cooling capacity of 2 W at 20 K. At the end of the cold head a Fe/Au thermocouple is mounted for measuring the temperature. A resistive heater is also mounted here for operation above the bottom end of the temperature range. To the cold head is attached a 7.0 in. long, 0.25-inch diameter copper rod by means of a threaded fitting. Thermal contact is enhanced by an indium gasket and conductive grease. At the end of the copper rod a 3.0 in. long, 0.094 in. diameter sapphire rod is appended. The sapphire was press fit into a hole of the same diameter in the copper rod and was further secured by wicking indium solder in between the sapphire and the copper. Sapphire was chosen as it is a good dielectric and thus does not interfere with the NMR experiment. At the same time it possesses good thermal conductivity at 20 K, a factor which facilitates the deposition of the sample at the tip of the rod. The error in temperature measurement due to the distance (~10 in.) between the thermocouple and sample was estimated by comparing the temperatures at which solid argon begins to pump off when deposited on either the sapphire rod or the cold head itself. The difference is between 6 and 8 K which places the sample within about 10 K of the measured temperatures in most cases.

The vacuum shroud surrounding the cold head is constructed of non-magnetic stainless steel, and a 0.5-in. ft cajon vacuum fitting is welded on at the bottom end. To this is attached a 0.5-in. glass tube blown onto 12 mm thin-wall NMR tubing, completing the vacuum shroud.

The spectra were taken at either 23.5- or 18.8-kg magnetic fields on a modified Varian XL-100-15 or a home-built spectrometer, respectively. The probe has previously been described.¹¹ It is a single-coil probe double tuned to ^{13}C and ^1H frequencies and produces a rotating field of 50-kHz at the ^1H frequency with 100 W of power. As the coil is just large enough to accept the NMR tube, a good filling factor is maintained while still allowing us to keep the high-power radiofrequency electronics at room temperature, greatly easing the refrigeration requirements. Field stabilization is achieved by using a D_2O external lock. Typically a mixing time of 2 ms and a recycle time of 3 s were used, although other conditions were required when significant deviations from ideality occurred in the powder pattern line shapes. Useful spectra can typically be obtained with 100 scans. On the other hand 500-1000 scans are usually accumulated, so that no sensitivity enhancement is needed thus preserving the true line shape. All chemical shifts were referenced by substituting either a sample of Me_4Si or a sample of the neat liquid for the solid sample and recording its spectrum under identical spectrometer conditions.

B. Sample Preparation. The gaseous samples were deposited either neat or were first mixed with argon (50/50) and allowed to stand overnight before deposition. The gas from the vacuum line passed through a calibrated leak valve and was deposited through a constricted piece of 0.25 in. glass blown onto the bottom of the NMR tube. The rate of deposition was monitored by periodically noting the decrease in pressure of a calibrated volume on the vacuum rack. After a sufficient amount had been deposited, the constriction was sealed and the cryostat closed off from the vacuum line. The low temperature maintained sufficient

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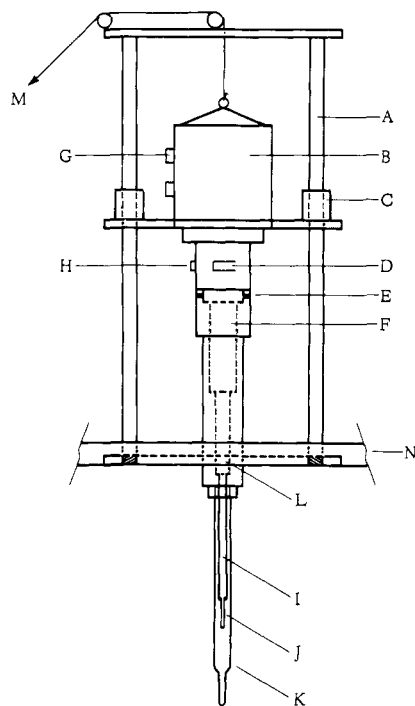


Figure 1. The cryostat assembly used for ¹³C NMR: (A) stainless-steel rods (of the 3 only 2 are shown for clarity); (B) Air Products duplex 202-B refrigeration unit mounted on aluminum table; (C) stainless-steel linear ball bearings to allow vertical motion of cryostat; (D) vacuum valve for pumpdown; (E) stainless-steel vacuum shroud; (F) 77 K cooling stage; (G) flexible hoses to refrigeration compressor; (H) instrumentation feed-through for heater and thermocouple; (I) 0.25-in diameter OFHC copper rod; (J) sapphire rod; (K) NMR tubing; (L) 10 K cooling stage; (M) counter weight; (N) mobile rack fabricated from an aluminum angle.

vacuum to keep the sample deposited on the sapphire rod thermally isolated from the glass envelope which is at room temperature. Samples were typically deposited on the sapphire rod until they were within 1.5–2.0 mm of the glass wall.

Cyclopropene and cyclobutene were deposited by transferring them into the bottom of the sealed NMR tube cooled with liquid nitrogen. The sapphire deposition rod was then cooled to the lowest attainable temperature, and the liquid nitrogen bath was replaced by a bath of the proper temperature to provide a reasonable rate of deposition. Due to the poor thermal conductivity and high heats of vaporization and fusion of the olefins of five carbons or greater, it was found necessary to co-deposit them with argon. This increased the thermal conductivity of the sample and allowed it to be kept at a much lower and more uniform temperature. Such a deposition was accomplished by placing the sample in a U-shaped tube at the end of the NMR tube and passing argon over the sample. The rate of deposition was again determined by the temperature of the bath in which the U-tube was immersed. The NMR tube was then sealed off as above.

The sample with its cryostat apparatus is mobile and may be wheeled to the spectrometer. The sample is lowered into the probe, currently by means of a pulley and counterbalance.

C. Chemicals. Research-grade ethylene, *cis*- and *trans*-2-butene, cyclohexane, cycloheptene, and *cis*-cyclooctene were purchased. Cyclopropene was purified by the method of Closs and Krantz.¹² The crude product was purified by bulb to bulb distillation through a series of cold traps at –80 and –95 °C. Purity was confirmed by IR spectroscopy.¹³ Cyclobutene was made according to Cope et al.¹⁴ Pyrolysis of the cyclobutene precursor was carried out at 50 torr instead of 100 torr to reduce isomerization of the product. Bulb to bulb distillation through two –80 °C baths was used to purify the product, and purity was again confirmed by IR.¹⁵ Cyclopentene was prepared and purified as described by Dehn and Jackson.¹⁶ Purity was established by liquid ¹³C NMR.

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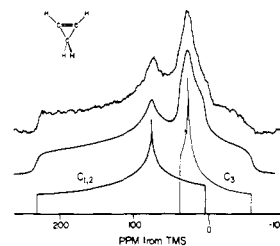


Figure 2. The experimental CP powder spectrum for cyclopropene taken at 25.16 MHz: upper, experimental spectrum; lower, the theoretical powder patterns for C₃ and C_{1,2}; middle, the sum of the patterns in the lower trace convolved with a Lorentzian broadening function whose full width at half-height is 4 ppm. Note that σ_{33} for C_{1,2} is still resolved even though it falls under the pattern for C₃.

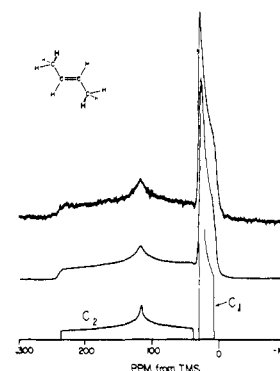


Figure 3. ¹³C powder spectrum of *trans*-2-butene: upper, experimental taken at 20.12 MHz; lower, theoretical patterns for C₁ and C₂ (the sharp upper portion of the pattern for C₂ was left off for clarity); middle, lowest trace convolved with 2 ppm Lorentzian. σ_{33} for C₂ is almost obscured by the broad base of the portion due to C₁.

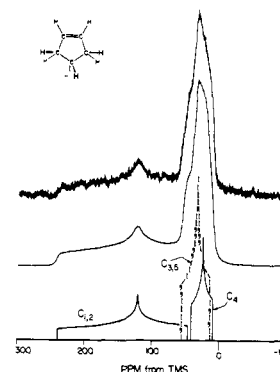


Figure 4. Comparison of theory and experiment for cyclopentene: upper, experimental CP spectrum at 20.12 MHz; Lower, the three contributing powder patterns; middle, sum of the three components in the lower trace convolved with a 2-ppm Lorentzian.

trans-Cyclooctene was obtained from Dr. R. Srinivasan.

III. Results

The spectra of cyclopropene, *trans*-2-butene, and cyclopentene shown in Figures 2–4 are typical of the results obtained for the molecules in this study. It is to be observed that the powder pattern for an olefinic carbon is dispersed over several hundred parts per million and a characteristic three component, asymmetric pattern is obtained. In several cases the spectral response of the aliphatic carbons overlaps the highest field component of the olefinic pattern. Often this component can be resolved if the aliphatic response is simple and is of low energy intensity not to obscure the olefinic breakpoint (Figures 2–4). When this is not the case, the component may be calculated from the two observed olefinic components and from the isotropic shift. These shift components for the olefins studied in this work are listed in Table I.

The tensor values were determined by comparing the experimental spectra with numerically calculated spectra which were

Table I.^{a, b} Tensorial and Average Chemical Shielding Constants for a Variety of Alkenes

compd	chem shifts		tensorial components		
	liquid ^d value	solid ^e value	σ_{11}	σ_{22}	σ_{33}
Olefinic carbons					
ethylene	123.3	126	234	120	24
<i>trans</i> -2-butene	126.0	127	232	113	37
<i>cis</i> -2-butene	124.6	124	232	119	22
<i>trans</i> -cyclooctene ^c	134.0		238	127	37 ± 5
<i>cis</i> -cyclooctene ^c	130.4		240	123	28 ± 5
cycloheptene ^c	132.7		245	126	27 ± 5
cyclohexene ^c	127.4		236	123	23 ± 5
cyclopentene	130.8	131	235	118	39
cyclobutene ^c	137.2		244	138	30 ± 5
cyclopropene	108.7	108	239	79	5
acetylene ^f	72.1	70	150	150	-90 ± 5
Aliphatic carbons					
<i>trans</i> -2-butene	17.6	20	27	27	5
<i>cis</i> -2-butene	12.1	13	28	6	6
<i>cis</i> -cyclooctene ^g C _α	26.0	13-42			
C _β	27.0				
C _γ	29.8				
<i>trans</i> -cyclooctene ^g C _α	35.5	21-60			
C _β	35.5				
C _γ	29.9				
cycloheptene ^g C _α	29.6	18-42			
C _β	28.0				
C _γ	32.7				
cyclohexene ^g C _α	25.7	11-38			
C _β	23.3				
cyclopentene C _α	32.8	31	52	30	12
C _β	23.3	23	39	22	7
cyclobutene	31.4	33	43	33	23
cyclopropene	2.3	3	40	29	-59

^a All shifts reported as ppm from Me₄Si. The estimated errors are ±2.5 ppm unless otherwise noted. Temperature of sample was ca. 30 K in all cases. ^b Solids shifts measured relative to external Me₄Si by sample substitution. Cyclohexene, cycloheptene, and *cis*-cyclooctene were measured relative to the neat liquid by sample substitution. The liquid was referenced to Me₄Si. ^c In these compounds σ_{33} was not resolved from the aliphatics and in this case was calculated from σ_{11} , σ_{22} , and the isotropic shift. ^d δ -(Me₄Si) = 193.7 - δ (CS₂) was used to convert the liquid data in ref 9 to the Me₄Si scale. Cyclopropene shifts were taken from ref 18. Acetylene shift is given in ref 17. ^e Single shift values indicate average of three measured tensorial values. A blank implies that one of the tensorial values could not be accurately determined and that the isotropic liquid value was used to calculate this indeterminate value (see *c* above). When the number of tensorial components was sufficiently large (two or more carbons) as to prevent this determination, only the range of tensorial values is given. ^f Tensorial shift values are taken from ref 8. σ_{33} was not discernible from the noise. As this molecule is linear, polarization transfer is very anisotropic and a hole appears in the solid line shape at the isotropic shift. With use of this value of 70 ppm for $\sigma_{\text{isotropic}}$, σ_{33} was then calculated. The 240-ppm overall anisotropy agrees very well with the 245-ppm value reported by Mohanty, *S. Chem. Phys. Lett.* 1973, 18, 581. ^g The various methylene shift tensors for these molecules were not resolvable. The range of possible tensor components is reported as the shift at 20% of the maximum intensity on either end of the band.

convolved with an appropriate Lorentzian broadening function. Typically the best fitting Lorentzian and a full width at half-height of about 2 ppm. While the calculated and experimental spectra are often superimposable, sometimes the intensities in the line shapes are distorted enough from ideality¹⁰ that the tensor values are taken as those that best fit the extremes and prominent central component of the band.

The intensity deviations from ideality do not seem to result from molecular reorientational averaging of the tensor. For example in the case of C₂H₄ the spectrum does not change over a twofold rise in temperature. One likely explanation for intensity deviations

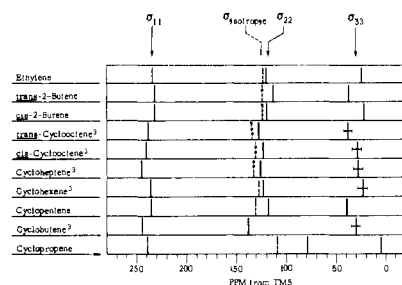


Figure 5. Graphical portrayal of the data in Table I for the olefinic carbons. The tensor elements can be seen to fall neatly into characteristic ranges. The greater range of tensor shifts when compared to the isotropic values is readily apparent. When errors are greater than ±2.5 ppm, they have been indicated with error bars.

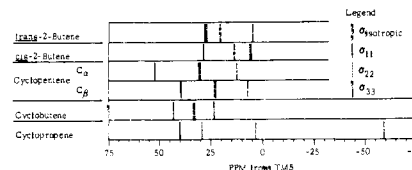


Figure 6. Tensor values for the aliphatics in Table I. Note that the deviation of σ_{33} for cyclopropene from the next closest tensor component is over 60 ppm.

is based on differences in the anisotropic relaxation of the protons and anisotropic polarization transfer. The possibility that such distortions may be instrumental has also not been entirely ruled out.

The tensor components for the aliphatic carbons in the olefins are also given. However, no attempt was made nor indeed can be made at the present time to deconvolve the tensors of the overlapping methylenes for the rings of six carbons or larger, and thus these values represent only the range of possible tensorial shift values for the several methylenes.

The data given in Table I and graphically portrayed in Figure 5 clearly illustrate the sensitivity of the olefinic carbon's tensor components to both structure and substitution. With the single exception of cyclopentene the trend in isotropic shifts parallels the values for σ_{22} . The two most uniquely shifted members of the series, cyclobutene and cyclopropene, whose σ_{22} values differ by 59 ppm, bracket the extremes of both the isotropic and σ_{22} shifts. The very high-field shift (79 ppm) for σ_{22} in cyclopropene constitutes one of the unique results in this study as it appears 33 ppm above the next closest σ_{22} component which is found in *trans*-butene. The two butenes and ethylene have rather similar σ_{22} values. For these three molecules σ_{22} and σ_{iso} both fall between the corresponding values for cyclopropene and most of the other cyclic olefins. At next lowest field we find the σ_{22} values for the 6-, 7-, and 8-membered rings, again paralleling the isotropic shifts. However, the overall spread in σ_{22} values is a factor of 2 larger than the spread in the isotropic shifts, therefore illustrating the greater sensitivity of the individual tensorial components to the details of molecular structure. It can be noted that the isotropic shifts also run parallel to trends existing in σ_{11} , the notable exception being cyclopropene. However, the overall range of shift recorded for σ_{11} in all compounds is only 13 ppm, and therefore this component is not very sensitive to structural change in the series. The σ_{33} component once again varies over a larger range of values, $\Delta\sigma_{33} = 34$ ppm. Inspection of Figure 3 demonstrates how variations in the three tensorial components can cancel each other and thereby reduce the overall range of isotropic shifts. This cancellation between components is especially evident in the values for σ_{11} and σ_{33} for several compounds in the series.

In the *cis-trans*-butene isomeric pair this cancellation of the σ 's is quite pronounced with a prominent downfield shift of 15 ppm noted in σ_{33} as the *trans* compound is compared with the *cis* isomer. Conversely the isotropic values measured in the liquid vary by only 1.4 ppm. The corresponding 9 ppm $\Delta\sigma_{33}$ found for the *cis-trans*-cyclooctene isomers again exceeds the 3.6 ppm value for $\Delta\sigma_{\text{iso}}$. These results clearly illustrate the point that one or more

tensorial shift values will generally be more sensitive to structural variations than is the σ_{160} shift which is a composite or average value. Statistically, average values invariably exhibit less vibration than found for the set of items used to calculate the average.

In the 2-butenes the methyls also reflect the cis-trans isomeric change in structure. In both isomers the tensors appear to be essentially axially symmetric, but they differ in that the unique component is downfield for the cis but upfield for the trans. Of course, the unique component is not necessarily identified as the component parallel to the methyl top axis. The structures of these molecules are such that three distinct components are to be expected in principle. The apparent axial symmetry may well result from coincidental degeneracy of two components which are different in the cis and in the trans compounds. Insufficient information exists at the present time to assign the methyl shift components to specific molecular geometries.

Except for one component in cyclopropene all of the tensorial values for the methylenes in the cyclic alkenes fall in the relatively narrow range of 5–52 ppm. The unique σ_{33} component in cyclopropene is –59 ppm, giving an overall anisotropy of –99 ppm ($\sigma_{33} - \sigma_{11}$) for the methylene in this compound. This anisotropy is the largest we know of for tetracoordinate carbon. At –59 ppm the σ_{33} shift is nearly as far upfield as the most shielded component (–90 ppm) of the sp carbon in acetylene.⁸ For all the other methylenes $|\sigma_{33} - \sigma_{11}|$ is less than 40 ppm.

IV. Discussion

In order to associate the various tensorial quantities recorded in Table I with specific geometrical features of the molecules, it is necessary to determine the orientation of principal axes of the shielding tensor in the molecular frame. For an asymmetric molecule with no symmetry features in the crystalline environment there is of course no way to do this solely from the experimental powder pattern. Whenever sufficient symmetry exists both in the molecule and in the immediate environment experienced by the molecule, then symmetry arguments may be sufficient to designate the orientation of the principal axes.

The D_{2h} molecular symmetry possessed by ethylene is sufficient to specify the shielding axes as parallel to the three C_2 rotation axes possessed by this molecule. This, of course, still begs the question of the effective symmetry of the crystalline environment of a given ethylene molecule. In principle, intermolecular shielding components can break the symmetry of intramolecular screening components and thereby invalidate simple molecular symmetry arguments used in a molecule even as simple as ethylene. As the ethylene shielding tensor has been observed to be the same within experimental error both in a neat solid and in a 1% matrix in argon,⁷ one can make the argument that the crystalline environment is probably not contributing any significant anisotropy to the shielding tensor for this one molecule. Isotropic intermolecular contributions are not distinguishable from bulk magnetic susceptibility corrections and therefore will not be of concern. These results, therefore, have led us to conclude that the three ethylene shielding components are associated with principal axes parallel to the three C_2 symmetry axes in ethylene.

Recently the orientation of the σ_{22} component reported in Table I has been shown experimentally to lie along the C=C bond axis in ethylene.⁸ This work used a doubly labeled ¹³C ethylene. The direct ¹³C–¹³C dipolar interaction defines a vector axis which can be clearly identified with the σ_{22} shielding component. The σ_{11} and σ_{33} components therefore lie perpendicular to the C=C bond vector. On the basis of theoretical arguments,¹⁷ the upfield component, σ_{33} , can be identified with the shielding axis which lies along the normal to the molecular plane. Thus, σ_{11} lies in the molecular plane but perpendicular to the C=C bond. A comparable ordering of tensorial components was noted by Kempf et al.¹⁸ in the somewhat related sp² carbonyl carbon of benzo-

phenone. Tokuhire et al.¹⁹ also have corroborative results in their theoretical calculations on formaldehyde. It is felt that the great similarity of component shifts between all the alkenes and the relatively large separation between the various components justify assigning a near ethylene shielding geometry to all molecules in this series. As the sp² hybridization in the molecules studies specifies a planar or nearly planar environment for the ethylenic carbon, the σ_{33} components are in each case assigned to the normal to this planar moiety. The orientation of the two in-plane components cannot be assigned solely on the basis of the local molecular symmetry. However the great similarity of σ_{11} shifts in all compounds including ethylene argues strongly for the σ_{11} axis having a similar orientation in all molecules. In that this is the in-plane axis perpendicular to the C=C bond in ethylene, we believe that the σ_{11} component in all molecules lies along an axis which will be perpendicular or nearly perpendicular to the carbon-carbon double bond. This leaves σ_{22} to be assigned to an axis which will generally lie along the double bond. We recognize that minor rotations of the two in-plane shielding axes away from these parallel and perpendicular axes may exist for all molecules other than ethylene and could make minor modifications in the tensor shielding values. In fact such variations between the axes of the shielding tensor and the appropriate bond vectors in the molecular frame may be the best way to account for the minor variations in σ_{11} and to some extent in σ_{22} . As indicated earlier in the discussion of ethylene shifts, intermolecular anisotropic shielding components could also affect all three components.

Having assigned a tentative geometry to all of the ethylenic shielding components in these molecules, the structural and electronic origins of the chemical shifts are now discussed briefly. To a first approximation the chemical shielding along any one axis depends upon the electrons located in p orbitals lying in the plane containing the shielded nuclei and perpendicular to the shielding axis. Thus, the chemical shielding along any direction in the molecule is really sampling information on the electronic structure perpendicular to the magnetic field axis. These geometrical features of chemical shielding provide a very intriguing three-dimensional characterization of electronic structure which should provide a critical test for the validity of proposed molecular wave functions or a promising way to refine quantum mechanical descriptions of the electronic structure of molecules.

The σ_{11} shielding component, associated with the in-plane perpendicular axis in ethylene, depends primarily on the carbon-carbon π and σ electrons. As this is the common moiety to all molecules studied in this series, perhaps it is not so surprising that this σ_{11} component exhibits the least dispersion. But even though this result might have been expected, its significance should not be missed: the σ and π electronic structure of carbon-carbon double bonds in an otherwise varied group of ethylenes must be remarkably similar.

The σ_{22} component along the double bond involves the magnetic field mixing of the π electrons with the carbon's σ electrons external to the double bond. This component will be significantly affected by the steric features associated with these external σ bonds. It should not be surprising therefore that the σ_{22} component is more dependent upon the unique changes in structure than the σ_{11} term because it is affected more by electrons in the differentiating structural moieties than is the σ_{11} component. It is especially interesting to note that $\Delta\sigma_{22}$ is only 8 ppm for *cis*-butene, cyclopentene, cyclohexene, cycloheptene, and *cis*-cyclooctene where the structural features are relatively similar about the double bond. Conversely $\Delta\sigma_{11}$ (13 ppm) and $\Delta\sigma_{33}$ (17 ppm) are both actually larger than $\Delta\sigma_{22}$.

The σ_{33} component involves only electrons located in the sp² hybrid orbitals appearing in the σ component of the double bond and in the external σ bonds. It is also noted that the σ_{33} shift falls right in the middle of the aliphatic chemical shift range. As aliphatic carbons only have σ electrons, these results on σ_{33} shifts establish a unity and consistency in carbon-13 shift correlations

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that lends very strong credence to the theoretical ordering of these shift components. The smaller range in the σ_{33} data vs. the corresponding σ_{22} values can be readily interpreted in terms of the greater polarizability of the π electrons important in the σ_{22} term. As chemical shielding depends upon processes of electron excitation by the magnetic field, there will be a magnification effect due to the π electrons in variations in σ_{22} over that of the all σ -electron σ_{33} term. As the σ_{11} term is affected by the same π -electron excitation processes and would manifest similar magnification effects, then the much narrower σ_{11} range further argues for the conclusions made above regarding the similarity between the members of this series in the σ - π -electron mixing which would also be important in σ_{11} .

Unlike the data on the olefinic carbons, the tensor quantities for the methyl and methylene carbons cannot be even tentatively identified at the present time with specific orientation of the molecule in the magnetic field. This is because one does not have a model system such as ethylene upon which to compare the various shift components for the alkyl carbon shifts. Furthermore, except for one component in cyclopropene, the various methylene components are much closer together in value and as such the order of the shifts for the various geometric orientations may not even be preserved from compound to compound. This narrower range of shifts also would allow anisotropic, remote shielding terms to play a relatively more important role both in the overall aliphatic shift magnitudes and in the ultimate orientation of the principal axes of the shift tensor. For these reasons no attempt is made to rationalize the various aliphatic shielding components in terms of specific molecular structural features. It is sufficient to draw

attention to the diversity of values observed in this study and to emphasize the ultimate importance such information may have in providing three-dimensional characterization of the electronic structure of molecules.

As the σ_{33} shift recorded for the methylene carbon in cyclopropene is sufficiently different, it does deserve some comment. This is especially the case since neither σ_{11} nor σ_{22} in cyclopropene are unusual when compared with the corresponding shifts in the other members of the series. Thus, it is seen that the anomalously high-field isotropic shift for the CH_2 in cyclopropene results from only one of the tensorial components appearing at a very high field. This observation provides a plausible explanation of the well-known high-field isotropic shifts recorded for this and other 3-membered rings.

In summary, ^{13}C tensorial shielding data for alkenes and cycloalkenes have been shown to provide a much richer source of structural information than the isotropic liquid shielding values. The information is directly related to the three-dimensional geometric and electronic structures of these molecules in such an intimate manner as to provide an interesting challenge for molecular quantum mechanic efforts at understanding small molecules.

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Dynamics of the Primary Events in Bacterial Photosynthesis

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Abstract: This paper considers the primary light-induced electron-transfer (ET) processes in the reaction center of photosynthetic bacteria which involved ET from the electronically excited state of the bacteriochlorophyll *a* dimer $(\text{BChl})_2$ to bacteriopheophytin (BPh) ((I.1)) and ET from BPh^- to ubiquinone (Q) ((I.2)). Ultrafast reactions I.1 and I.2, which are practically temperature independent over the range 4–300 K, cannot be accounted for in terms of low-temperature nuclear tunnelling through a nuclear barrier, as such a mechanism would imply an unrealistically high characteristic molecular frequency for the electron-donor and the electron-acceptor centers. Two mechanisms for ultrashort, temperature-independent processes I.1 and I.2 were examined. The rate of the ET reaction (I.2) is considerably longer than characteristic medium-induced vibrational relaxation rates, so that process I.2 has to occur from a thermally equilibrated nuclear configuration of $\text{BPh}^- \cdot \text{Q}$. Reaction I.2 is assigned to an activationless nonadiabatic ET process, the short lifetimes for this reaction stemming from a large value of the electronic coupling $V \approx 4 \text{ cm}^{-1}$ which, according to rough estimates, implies that the average $\text{BPh}^- \cdot \text{Q}$ spacing is $\sim 10 \text{ \AA}$. We propose that the ultrafast reaction (I.1) occurs from a nonequilibrium nuclear configuration of the $(\text{BChl})_2 \cdot \text{BPh}$ initially excited state which is located above the crossing point of the nuclear potential surfaces for $(\text{BChl})_2 \cdot \text{BPh}$ and for $(\text{BChl})_2^+ \cdot \text{BPh}^-$. Such a novel ET mechanism involves competition between ET and vibrational relaxation. A theory has been developed to handle this problem and applied to reaction I.1. A microscopic molecular scheme for the primary events of charge separation in bacterial photosynthesis is proposed, which rests on the optimization of (a) the intramolecular distortions of the equilibrium nuclear configurations (these nuclear distortions determine the vibrational overlap contributions to the ET rates) and (b) the intermolecular spatial organization of the donor and the acceptor (the donor-acceptor separation (and orientation) determines the electronic coupling which dominates the preexponential contribution to the ET rate). The molecular scheme is successful in accounting for the qualitative and the quantitative features of the primary ET rates and in providing a picture for the directionality, selectivity, and efficiency of the charge separation events.

I. Introduction

The understanding of the primary events in bacterial photosynthesis is of central importance for the elucidation of the basic mechanisms of the acquisition, storage, and disposal of energy in the photosynthetic process.¹ Photosynthetic bacteria, like green

plants, contain an antenna system that transfers the excitation energy to the reaction center where charge separation occurs. By a suitable chemical treatment of the bacterial chromatophores the reaction center can be isolated from the antenna pigments.^{2,3} During the last few years extensive new information on the dynamics of charge separation in such "isolated" reaction centers has emerged from experimental studies, utilizing the modern techniques of ultrafast picosecond spectroscopy.⁴⁻¹¹ Indeed, the

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