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Structure of Spiropentane: An NMR Study

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Abstract: The high resolution ^{1}H NMR spectrum of spiropentane in an orienting liquid crystal has been recorded and analyzed in terms of both indirect and direct coupling constants. The interring J_{HH}[4] are reported here for the first time. The direct coupling constants from the present and a previous liquid crystal study have been corrected for harmonic vibrational motion and used to calculate proton distance ratios. Furthermore, previous electron diffraction distances have also been corrected for harmonic vibrational motion and used to scale the proton ratios. Comparison of the three sets of structural information indicates that while the NMR results are essentially equivalent, the electron diffraction H-C-H angle is considerably larger. The NMR values are much closer to those from both theoretical calculations and cyclopropyl fragments of similar molecules.

Spirohydrocarbons have been the subject of numerous detailed theoretical studies of structure, energy, strain, and π-electron delocalization.[1] However, experimental structural information has been limited to electron diffraction and liquid crystal NMR studies of spiropentane and electron diffraction of spiro[2.4]hepta-4,6-diene.[2-4] Precise experimental observations are desirable in confirming the assumptions and conclusions of ab initio and semiempirical methods, which, if reliable, can give valuable insights into the properties of known compounds as well as predictions of hypothetical ones.

Electron diffraction has proved to be a valuable technique in determining heavy-atom coordinates, but radial distribution curves often yield poorly defined carbon-hydrogen distances. Furthermore, in order to reduce the total number of parameters, the least-squares analyses may be limited to averages of carbon-hydrogen bonds.[5] Conversely, liquid crystal NMR can achieve excellent precision in proton distance ratio,[6] though skeletal information is unobtainable unless carbon-13 satellite spectra can be observed. A combination of the two techniques has thus proved successful in defining the total molecular structure in some cases.[7]

Such a combined NMR approach has been previously attempted with spiropentane, but the results were not internally consistent.[3] In the electron diffraction study of Dallinga et al., the four equivalent H-C-H bond angles were found to be 118.4 ± 0.90°,[2] whereas liquid crystal NMR, using the electron diffraction carbon coordinates and C-H bond lengths, found the angle to be 115° 13′.[3] In later ab initio calculations, Kao et al. predicted the angle to be 113.9°.[8] The authors found the discrepancy with electron diffraction results surprising, as much better agreement between the methods had been found for the comparable H-C-H angles in spiro[2.4]hepta-4,6-diene. The above authors did not cite maximum overlap calculations which yielded an angle of 114° 33′.[9]

Table I. Typical NMR Parameters for Spiropentane in Phase IV

	direct couplings^{a,c}		indirect couplings^{b,c}
D_{12}	761.144 + 0.006	J_{12}	−3.793 + 0.043
D_{13}	294.531 + 0.009	J_{13}	8.741 + 0.041
D_{14}	158.349 + 0.008	J_{14}	5.073 + 0.022
D_{15}	−304.247 + 0.010	J_{15}	−0.258 + 0.041
D_{16}	−87.590 + 0.005	J_{16}	−0.478 + 0.022
D_{18}	−29.945 + 0.009	J_{18}	0.870 + 0.022
rms error	0.112		
lines assigned	99		

^{a} Errors are probable errors as calculated by LAOCN3. ^{b} Errors are the standard deviations of five sets. ^{c} Couplings are in units of hertz.

One possible explanation for the discrepancies may be the omission of vibrational corrections to the experimental results, as inclusion of harmonic corrections is known to be essential when comparing results of different methods.[10] For example, the H-C-H angle of cyclopropane was found equal in liquid and gas phases, within experimental limits, only after application of such corrections.[11]

The complete normal coordinate analysis of spiropentane has appeared subsequent to the two experimental studies cited above,[12] and has been used by us in the present investigation to apply vibrational corrections in the hope of resolving the differences. Further corroborating evidence has also been supplied by the

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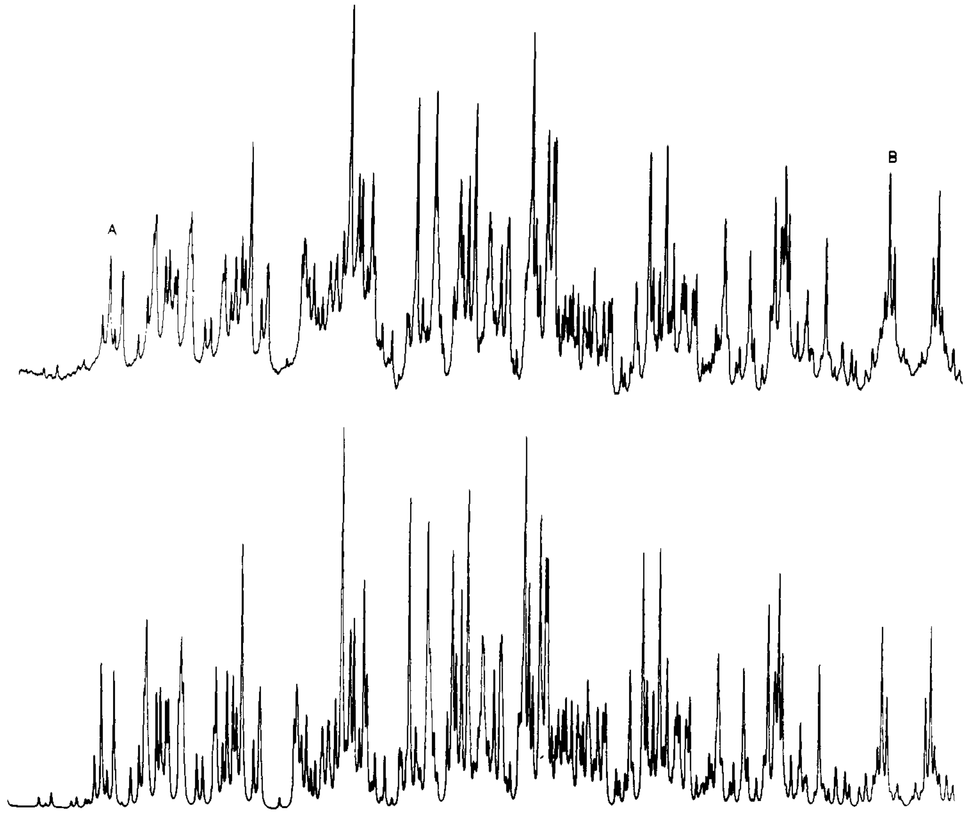

Figure 1. Observed and calculated proton spectrum of spiropentane in Merck Phase IV. Downfield half of symmetric pattern: A, -1226.9 Hz, B -114.2 Hz.

analysis of spiropentane in a separate liquid crystal medium.

Experimental Section

Spiropentane was purchased from Chemsamp Co. and used without further purification. Proton spectra were obtained for 6.9 wt % solutions in Merck Phase IV, using a Bruker CXP-300 superconducting NMR spectrometer. Merck Phase IV is a nematic thermotropic liquid crystal which spontaneously orients in magnetic fields at room temperature. Five spectra of 25 scans each were acquired by using 16K real points at a probe temperature of 301 K. Spectral widths of 4500 Hz gave a digital resolution of 0.274 Hz and line widths were about 2.5 Hz at half-height. A sample spectrum of the downfield half of the pattern, with the corresponding computer fit, is shown in Figure 1.

Results

Spectral analyses were performed with the aid of the program LAOCN3 modified for direct coupling constants. Initial values for the indirect couplings were taken from the literature.[13] During the least-squares analysis both indirect and direct couplings were iterated upon, yielding the values in Table I.

Previously, only the intraring indirect couplings determined from isotropic analysis have been reported and these exhibited relatively high associated error.[13] The indirect couplings found in the present study, which are the averages from five spectra, possess low standard deviations and indicate significant coupling between interring protons. The probable errors as calculated by LAOCN3 were consistently lower than the reported errors. Intraring couplings in the present study are equivalent to previous values within experimental limits.

Distances computed from direct coupling constants (R_d) are known to deviate from the equilibrium values (R_e) as a result of both anharmonic and harmonic vibrational motions. While the former effect cannot easily be corrected for, the latter, with suitable harmonic force fields, can be eliminated to give the distance parameter R_α. The R_α distances are suitable for comparison with results obtained by other experimental methods.[14] For spiropentane, harmonic vibrational averaging of the direct coupling constants was performed by the methods of Lucas, employing the programs NCAMS[15] and SHAPE,[16] modified to include the vibrational corrections. The force field of Cyvin and Gebhardt was used with one alteration.[12] While the force constants for the A_2, B_1, B_2, and E species correctly reproduced the exact published frequencies, those for the A_1 class were in error until the S_5 diagonal force constant was changed from 0.05 to 0.50.

Table II. Corrections for Harmonic Vibrations for Spiropentane

direct coupling[a]	previous NMR[b]	Phase IV
D_{12}	-38.133	-35.973
D_{13}	-3.678	-3.469
D_{14}	-3.724	-3.513
D_{15}	-5.228	-4.932
D_{16}	0.273	0.257
D_{18}	0.489	0.461

[a] In units of hertz. [b] Uncorrected direct couplings from ref 3.

Distances determined from electron diffraction radial distribution curves (R_a) also differ from equilibrium distances because of contributions from both anharmonic and harmonic vibrational motion. The latter effect was again corrected for by the methods of Lucas,[11] to give the corresponding R_α values.

Discussion

Interpretation of the interring indirect coupling constants is difficult, due to the complexity of the mechanisms which contribute to four-bond couplings. While the $J_{HH}{}^4$ are known to vary over an extremely large range (-1 to +18 Hz), most are of the approximate size observed for spiropentane, -0.5-1.0 Hz.[17] Two main mechanisms are believed to contribute to the coupling, a

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Table III. Final Distance Ratios for Spiropentane in Phase IV and EBBA

ratio	Phase IV[a]	previous NMR[b,c]	% difference[d]
	Uncorrected		
r_{13}/r_{12}	1.3697 ± 0.0001	1.3765 ± 0.0004	−0.50
r_{14}/r_{12}	1.6959 ± 0.0001	1.7014 ± 0.0004	−0.32
r_{15}/r_{12}	1.6895 ± 0.0002	1.6983 ± 0.0005	−0.52
r_{16}/r_{12}	2.0553 ± 0.0002	2.0641 ± 0.0005	−0.43
r_{18}/r_{12}	2.3651 ± 0.0002	2.3742 ± 0.0005	−0.38
S_{zz}[e]	0.0390 ± 0.0001	0.0412 ± 0.0003	
rms error	1.4810	1.3497	
	Corrected		
r_{13}/r_{12}	1.3858 ± 0.0001	1.3922 ± 0.0004	−0.46
r_{14}/r_{12}	1.7089 ± 0.0001	1.7141 ± 0.0004	−0.30
r_{15}/r_{12}	1.7235 ± 0.0001	1.7321 ± 0.0005	−0.50
r_{16}/r_{12}	2.0871 ± 0.0001	2.0958 ± 0.0005	−0.42
r_{18}/r_{12}	2.3962 ± 0.0001	2.4051 ± 0.0005	−0.37
S_{zz}	0.0398 ± 0.0001	0.0420 ± 0.0003	
rms error	1.0730	0.9225	

[a] Weightings of direct couplings by probable errors from LAOCN3. [b] Equal weightings. [c] Direct couplings from ref 3. [d] % deviation is defined as 100×(NMR1 − NMR2)×2/(NMR1 + NMR2). [e] Calculated by using the vibrationally corrected electron diffraction C-H bond length (1.077 Å) and carbon coordinates.

small negative "indirect", or "throughbond", interaction, and, when spatially favorable, a larger positive, "direct" mechanism.[18] The direct mechanism is normally operating when the rear lobes of the C–H hybrid orbitals containing the interacting spins are pointed toward each other.[19] In spiropentane, the only hybrids approaching this geometric arrangement are those for the 1 and 8 protons, which may explain the positive value for the coupling.

Examination of the results in Table III indicates that differences in distance ratios between the liquid crystal phases are 0.5% or less, about the same variation observed for aromatic structures obtained by the NMR method.[6,15] The vibrational corrections to the distance ratios are often sizable, the largest changes being about 1.5%. The errors in the NMR distance ratios are reported as the standard deviations of five sets, and do not reflect systematic errors. Quantitative assessment of the latter is difficult, but a number of sources can be located. First, as the magnitudes of the corrections are large, errors in the force field should be transmitted to those of the distance ratios. We have attempted to estimate the sensitivity of the distance ratios to force constants by arbitrarily raising the diagonal elements of the force constant matrix by 5.0%. In all cases, changes in the distance ratios were less than 10^{-3} and were typically on the order of the experimental error.

Further uncertainty arises due to the possibly erroneous assumption that the molecular geometry is independent of orientation. Evidence for such a dependence is known from the spectra of tetrahedral molecules, which show dipolar fine structure when none is expected on the basis of symmetry.[20,21] The dipolar couplings can be accounted for by incorporating distortions of less than 0.1° in the angles.[21] Several recent theoretical treatments have also claimed that the dipolar couplings can be accounted for without geometrical distortions.[22,23]

Corrections to the electron diffraction distances are generally small in comparison with experimental errors, but are important in the case of the directly bonded C–H. In spiropentane the correction to the C–H is 0.014 Å, and the corrected value of 1.077 Å turns out to be very close to the value for cyclopropane, 1.079 ± 0.003 Å. Significantly, the corrected value is now closer to the ab initio value, 1.082 Å.

Table IV. Comparison of Structural Information for Spiropentane by Different Methods

	proton distances		
	Phase IV[a]	previous NMR[a,b]	ED[c]
r_{12}	1.817 ± 0.003	1.812 ± 0.003	1.860 ± 0.007
r_{13}	2.518 ± 0.004	2.523 ± 0.004	2.467 ± 0.033
r_{14}	3.105 ± 0.006	3.106 ± 0.006	3.090 ± 0.026
r_{15}	3.131 ± 0.006	3.138 ± 0.006	3.139 ± 0.042
r_{16}	3.792 ± 0.007	3.797 ± 0.008	3.801 ± 0.037
r_{18}	4.353 ± 0.008	4.358 ± 0.008	4.364 ± 0.034

H-C-H, deg				
Phase IV[a]	previous NMR[a,b]	ED[c]	ab initio[d]	max overlap[e]
115.0 ± 0.7	114.5 ± 0.7	119.4 ± 1.1	113.9	114.6

[a] Calculated by using vibrationally corrected electron diffraction C-H bond length (1.077 Å) and carbon coordinates. [b] Direct couplings from ref 3. [c] Uncorrected distances from ref 2. [d] Reference 8. [e] Reference 9.

The corrected electron diffraction C–C and C–H bond lengths were used to scale the NMR distance ratios, and the results from all three methods are compared in Table IV. The revised errors in the NMR parameters are our best estimates and are judged to include the effects arising from the previous average errors associated with electron diffraction in scaling and the abovementioned systematic error. The final errors shown are probably overly generous, but have been estimated conservatively in the interest of meaningful comparison with electron diffraction and theoretical results. It can be seen that, after the vibrational corrections, NMR distances from the two studies are equal, within experimental error, as are several of the electron-diffraction values. However, the geminal R_{12} still differs by over 2.5% from either of the NMR distances, which is reflected most clearly in the larger H–C–H bond angle.

Although molecular structures determined by methods using different phases, i.e., liquid and gas, need not in general be the same, the magnitudes of the differences in the present case seem unusually large, as the structure of cyclopropane was practically invariant to the phase. The reproducibility of the values in a separate liquid crystal medium appears to confirm the condensed phase bond angle values.

For theoretical calculations, the vibrationally corrected NMR H–C–H angles are closest to those determined by the method of maximum overlap, which is intermediate between the two. The ab initio angle is within the error of the EBBA value, but lower than that in Phase IV. The ab initio method may systematically underestimate the angle, as can be seen with cyclopropane, which was also lower by over 1°. The cited agreement with spiro[2.4]hepta-2,6-diene may be incorrect, if one assumes that the change in the H–C–H angle from vibrational correction of the electron diffraction distances is of the same order of magnitude as those for cyclopropane and spiropentane.

Comparison of the H–C–H angles for spiropentane with cyclopropyl fragments in similar structures is also instructive. The model cyclopropane (115.8° ± 1.0, 115.15°)[11] and bicyclo[1.1.0]butane (115.6°)[24] agree well with the NMR values for spiropentane, while bicyclo[2.1.0]pentane (116.7 ± 0.1°)[25] is somewhat larger.

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