Theor Chim Acta (1985) 68: 421-430

THEORETICA CHIMICA ACTA

Low temperature ^{13}C NMR magnetic resonance in solids 4. Cyclopropane, bicyclo[1.1.0]butane and [1.1.1] propellane*

Anita M. Orendt[1], Julio C. Facelli[1], David M. Grant[1], Josef Michl[1], Fredrick H. Walker[2], William P. Dailey[2], Sherman T. Waddell[2], Kenneth B. Wiberg[2], Michael Schindler[3] and Werner Kutzelnigg[3]

[1] Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, USA
[2] Department of Chemistry, Yale University, New Haven, Connecticut 06511, USA
[3] Lehrstuhl fur Theoretische Chemie Ruhr-Universität, D-4630 Bochum, Federal Republic of Germany

(Received May 20/Accepted June 3, 1985)

The solid state ^{13}C NMR spectra of bicyclo[1.1.0]butane and [1.1.1]propellane have been measured at low temperature. The orientation of the principal axes of the chemical shielding tensor have been determined with ab initio calculations based on the IGLO (Individual Gauge for Localized Orbitals) method when they are not determined by symmetry. Excellent agreement is obtained between the calculated and experimental principal values of the shielding tensor when basis sets containing polarization functions are used. In most cases the agreement is such that the calculated values are within the experimental error.

Key words: Chemical shift anisotropy — Highly strained compounds — Quantum chemical calculation of shielding tensors

1. Introduction

Due to its unique structure, [1.1.1]propellane has been the focus of several theoretical studies [1-4]. The geometry at the bridgehead carbons is inverted,

---

* Part 3 of this series: Ref. [7]

i.e., all the attached groups lie in one hemisphere. A review article dealing with the chemistry of compounds containing atoms with inverted geometries has recently been published [5].

Although theoretical studies have made the intriguing finding that there is very little difference charge density attributable to the presence of the central C-C bond [1-3], the bonds in [1.1.1]propellane appear to be surprisingly normal. The C-C and C-H bond lengths are very similar to those in cyclopropane, and the vibrational spectrum shows a strong antisymmetric C-C stretch at about 530 cm^{-1} and a force constant for the central C-C bond similar to that of the other C-C bonds [6].

The one striking difference with respect to more usual cyclopropane rings is observed in ^{13}C NMR. Along the series cyclopropane, bicyclobutane, and [1.1.1]propellane, there is a large change in the ^{13}C isotropic chemical shift of the CH_2 carbon. In cyclopropane the shift is -4 ppm from TMS [7], in bicyclobutane 33 ppm [8], and in [1.1.1]propellane 74 ppm [9].

This observation suggested that a solid state ^{13}C NMR comparison of these three compounds would be worthwhile. Chemical shielding tensors can be much more useful than just the isotropic shifts because up to three times more information can be obtained. Combination of the experimental results with the results of *ab initio* calculations allows the tentative assignment of the orientation of the principal axes in the molecular frame [10]. With these assignments information about the electronic environment in the plane perpendicular to each axis can be obtained, and this may eventually provide a better understanding of the nature of the bonding in the vicinity of the central C-C bond in [1.1.1]propellane and related strained organic molecules.

2. Experimental and computational methods

Solid state ^{13}C NMR spectra of neat [1.1.1]propellane [9] and neat bicyclobutane [11] were taken at a temperature of approximately 20 K using an Air Products Model 202-B closed cycle helium refrigerator [12]. Spectra were recorded using the cross-polarization method [13] on a home-built spectrometer [12] operating at a ^{13}C frequency of 20.12 MHz. Contact times of 3 ms and recycle times of 3 s were used. The experimental results for cyclopropane were obtained previously [7] in this laboratory. Experimental shieldings are referenced to an external sample of TMS as described previously [12]. The experimental spectra were analyzed by direct simulation [12] and comparison with experiment. An error of 2-5 ppm is estimated in the reported values.

The *ab initio* calculations were performed using the IGLO method [14-17], based on the coupled Hartree-Fock perturbation theory with localized molecular orbitals. Huzinaga [18] Gaussian basis sets were used in the calculations as follows:

Basis I: C (6, 3) contracted to (411, 21)
H (3) contracted to (21)

Basis II: C (7, 3) contracted to (4111, 21)
H (3) contracted to (21)
Basis III: C (9, 5, 1) contracted to (51111, 311, 1)
H (5, 1) contracted to (311, 1)
Basis IV: C (9, 5, 1) contracted to (51111, 2111, 1)
H (5, 1) contracted to (311, 1).

In the last two basis sets the exponent of the *d* orbitals on the carbons was 1.0 and the exponent for the *p* orbitals on the hydrogens was 0.7. Basis set II is of double zeta quality. Experimental geometries used for the calculations were obtained from the following references: cyclopropane [19], bicyclobutane [20], and [1.1.1]propellane [6]. For comparison with the experimental results, the principal values of the calculated shielding tensor were converted to the TMS scale assuming that CH_4 and TMS have the same isotropic chemical shift. This assumption is supported by IGLO calculations for CH_4 and TMS [16] and by the small difference (between 3 and 5 ppm) found between their experimental chemical shifts in solution [21]. Absolute shielding values of 211, 219, 214, and 199 ppm were used for CH_4 in the conversion for basis sets I through IV, respectively. Calculations using basis sets I and II were done on a VAX 11/750, whereas those using basis sets III and IV were done on a CYBER 205.

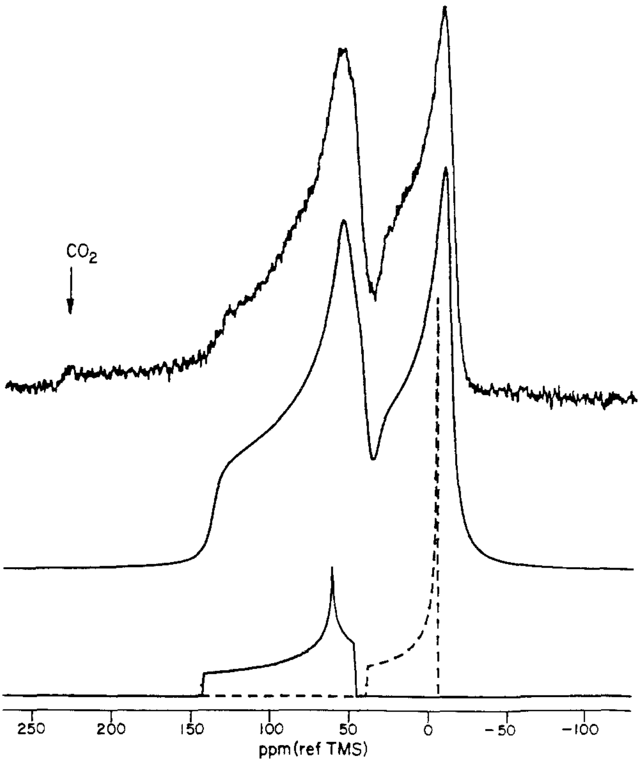

Fig. 1. Spectra of [1.1.1]propellane. Top to bottom: experimental, theoretical convoluted with a Lorentzian broadening function, and theoretical. The weak downfield signal is due to a CO_2 impurity

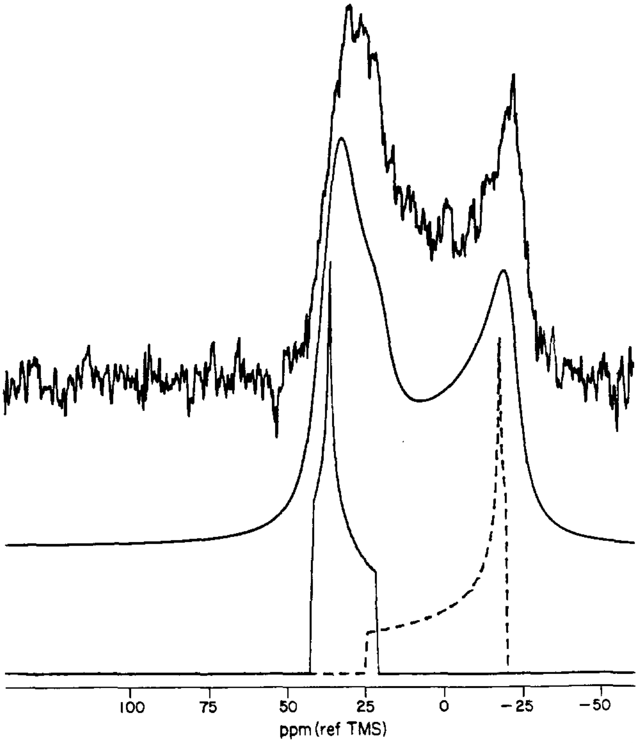

Fig. 2. Spectra of bicyclobutane. Top to bottom: experimental, theoretical convoluted with a Lorentzian broadening function, and theoretical

3. Results and discussion

The spectra of [1.1.1]propellane and bicyclobutane along with the computer simulations are shown in Figs. 1 and 2, respectively. The calculated shielding tensors are compared with the experimental results in Table 1. The principal values calculated using basis IV agree well with the experiment. The total molecular energies calculated at each of the four basis levels are listed in Table 2, along with literature values. The energies calculated indicate the importance of using polarization functions in dealing with these highly strained systems, as previous workers have shown [1, 24]. Between bases II and III there is a noticeable decrease in the total energy.

The calculation of the principal components is even more sensitive to the changes in the basis set. This is especially evident from the changes between bases III and IV, which differ only in the contraction of the p orbitals on the carbon. While most of the components are very sensitive to basis set changes, there are exceptions, such as the $\sigma_{\parallel}$ component of the bicyclobutane CH carbon. Also the trend is for the calculated results to agree better with the experiment when the basis set size increases, with the notable exception being the $\sigma_{A'}$ component for the CH_2 carbon of bicyclobutane.

Table 1. ^{13}C shielding tensors of cyclopropane, bicyclobutane and propellane[a]

	Calculated				Experimental
Basis Set	I	II	III	IV	
Cyclopropane[b,c]					
σ_A	35	30	25	27	22
σ_B	−8	−9	6	9	2
σ_C	−15	−23	−40	−40	−36
σ_{iso}	4.0	−0.7	−3.0	−1.3	−4.0
σ_{liq}					−2.8
Bicyclobutane CH_2[d]					
$\sigma_{A'}$	23	21	8	10	(20)
σ_B	27	22	37	38	(35)
$\sigma_{C'}$	60	55	42	43	(41)
δ	48°	48°	57°	56°	
σ_{iso}	36.7	32.7	29.0	30.3	32.0
σ_{liq}					33[e]
Bicyclobutane CH[d]					
$\sigma_{\parallel}$	32	31	30	32	(23)
$\sigma_{\perp}$	−8	−17	−23	−24	(−19)
$\sigma_{\perp'}$	−2	−10	−26	−26	(−21)
δ'	8°	6°	−5°	−6°	
σ_{iso}	7.3	1.3	−6.3	−6.0	−5.7
σ_{liq}					−3.0[e]
[1.1.1]Propellane CH_2[b]					
σ_A	55	53	42	43	(43)
σ_B	37	43	49	53	(57)
σ_C	154	151	133	138	(138)
σ_{iso}	82.0	82.0	74.3	78.0	79.3
σ_{liq}					74.2[f]
[1.1.1]Propellane C[g]					
$\sigma_{\parallel}$	40	36	26	30	35
$\sigma_{\perp}$	24	14	−6	−11	−11
σ_{iso}	29.3	21.3	4.7	2.7	4.3
σ_{liq}					1.0[f]

[a] Shielding values in ppm, experimental values referenced to TMS, calculated values to CH_4 as is explained in the text. Basis set levels as explained in the text. The experimental values shown between brackets are those in which only the principal values are known

[b] σ_A: bisecting the HCH angle, σ_B perpendicular to the HCH plane and σ_C perpendicular to the CCC plane

[c] Experimental values are taken from Ref. [7]

[d] The orientation of these components and the definition of the angles δ and δ' are shown in Fig. 3. Positive angles mean counterclockwise rotation

[e] From Ref. [8]

[f] From Ref. [9]

[g] $\sigma_{\parallel}$: parallel to the central C–C bond, $\sigma_{\perp}$: degenerate component perpendicular to this bond

Whereas this is the first calculation of the shielding tensors in bicyclobutane and [1.1.1]propellane, there have been Coupled Hartree-Fock (CHF) calculations done for cyclopropane using an extended basis set [22]. A comparison of our results with the previous ones is made in Table 3. The values reported are absolute

Table 2. Total energies

Compound	Basis Set	Energy (a.u.)
Cyclopropane	I	−116.8382
	II	−116.8825
	III	−117.0858
	IV	−117.0859
	6-31G*/6-31G**[a]	−117.0691
	1172/51 contracted	
	(651/31)[b]	−117.0891
	(1161/51) contracted	
	(531/31)[c]	−117.0981
Bicyclobutane	I	−154.5651
	II	−154.6384
	III	−154.9025
	IV	−154.9028
	6-31G*/6-31G**[a]	−154.8824
[1.1.1]Propellane	I	−192.2825
	II	−192.3877
	III	−192.7251
	IV	−192.7256
	6-31G*/6-31G**[a]	−192.7011

[a] Values taken from Ref. 1. Calculations used the 6-31G** basis set after geometry optimization was done with the 6-31G* basis set

[b] From Ref. [22]

[c] From Ref. [23]. This is the best SCF energy calculated to date

Table 3. Comparison of absolute shieldings in cyclopropane

Basis Set	σ_{11}	σ_{22}	σ_{33}
I	169	213	221
II	182	221	237
III	189	208	254
IV	172	190	239
(1172/51) contracted			
(651/31)[a]	172	187	233

[a] From Ref. [22]

shieldings, or shift values with respect to the bare carbon nucleus. Table 3 confirms that for sufficiently large basis sets both conventional CHF and the IGLO method converge to the same results. However the IGLO results approach the final values already with much smaller basis sets than do the CHF results [14–16]. As a result, the IGLO method requires much less computational effort and it can be easily applied to much larger systems.

The calculations provide for an assignment of the principal axis system of the ^{13}C shielding tensor into the molecular frame. In molecules with sufficient symmetry the directions of one or more of the principal axes are defined [25], but the assignments of the three components to these axes may be still undetermined experimentally unless the ^{13}C under consideration lies on a symmetry axis of order 3 or greater. Experimentally, this information can be obtained in one of three ways: single crystal studies [13], study of doubly labeled materials [26], or by a two-dimensional powder technique [27].

The orientation for doubly labeled cyclopropane was determined previously with the use of dipolar spectroscopy [7]. The downfield component, σ_{11}, was found to bisect the CH_2 group; σ_{22} was assigned to be the component perpendicular to the CH_2 plane and the upfield component, σ_{33}, was the component perpendicular to the carbon ring. This assignment was reproduced by the calculations at all basis set levels.

For the CH_2 carbons of bicyclobutane and [1.1.1]propellane only the calculated orientation of the shielding tensors is known. As in the case of cyclopropane, the orientation of the principal axes in [1.1.1]propellane is set by the molecular symmetry. The calculations assign σ_{11} to be the component perpendicular to the local CCC plane in all basis sets. This component, perpendicular to the cyclopropane ring unit, has changed from the furthest upfield in cyclopropane to the furthest downfield in [1.1.1]propellane, with an extraordinary net change of 174 ppm. In the calculations with bases III and IV, σ_{22} is the component perpendicular to the HCH plane and σ_{33} is the component bisecting the CH_2 angle. However, bases I and II give the reverse order. This is somewhat disturbing as in previous experience with the IGLO method the calculated orientation has been insensitive to basis set size; furthermore, we have never seen previously a reordering of the components between different basis sets. A possible explanation is that this reorientation of σ_{22} and σ_{33} may be another indication of the crucial role played by polarization functions in dealing with highly strained molecules. Also, this reordering may not be meaningful since the calculated differences of σ_{22} and σ_{33} are barely outside of experimental error.

For the methylene carbon of bicyclobutane the only direction fixed by symmetry is the component perpendicular to the HCH symmetry plane of the molecule. This component is calculated to be the σ_{22} at all basis levels. The calculated orientation of σ_{11} and σ_{33} is shown in Table 1 and in Fig. 3. Due to the magnitude of the angle δ between $\sigma_{A'}$ and the direction bisecting the HCH angle, neither $\sigma_{A'}$ nor $\sigma_{C'}$ can be associated with the component that bisects the HCH angle or the component perpendicular to the local CCC plane. It should be noted that this is an unusual situation; in most previous studies the local symmetry had always dictated the principal axes of the shielding tensor.

The C_3 axis passing through the quarternary carbon of [1.1.1]propellane makes this the only carbon in this study for which an assignment of the shielding components can be made on the basis of symmetry directly from the natural abundance powder spectrum. The spectrum in Fig. 1 clearly shows an axially symmetric band with the α_{11} component parallel to the central C–C bond; the other two degenerate components therefore lie perpendicular to this axis. The calculations reproduce this result at all basis set levels.

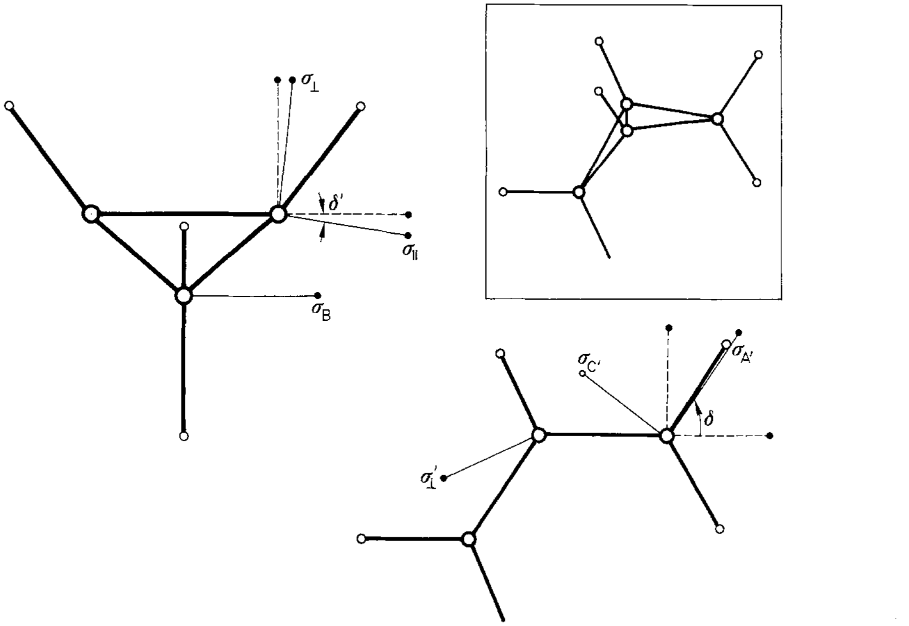

Fig. 3. Principal axis systems for the carbon atoms of bicyclobutane. The view on the *upper left* is perpendicular to the H–C–C–H plane while that on the *lower right* is perpendicular to the plane of the CH_2 groups

Finally, for the CH carbon of bicyclobutane the symmetry plane containing the central C–C bond requires that the direction of one of the principal axes be perpendicular to the H–C–C–H plane. The experimental results for the CH carbon of bicyclobutane indicate that σ_{22} and σ_{33} are almost degenerate, with σ_{11} 43 ppm further downfield. At all basis set levels used, σ_{11} lies close to the C–C axis; the angle of deviation from this bond, δ', is shown in Table 1 and Fig. 3. The component that lies perpendicular to the H–C–C–H plane is σ_{22} in bases I and II, while in bases III and IV it is determined to be σ_{33}.

4. Conclusions

The shifts in the principal values of the shielding tensor of the CH_2 carbons in going from cyclopropane to [1.1.1]propellane are even more dramatic than the change of 78 ppm in the isotropic shifts. Most of this downfield shift is due to the change of 174 ppm in the component perpendicular to the local CCC plane. The other two components also shift downfield, but by much smaller amounts. The entire change is in the paramagnetic contributions.

In the IGLO method the shielding is divided into bond contributions [17]. From cyclopropane to [1.1.1]propellane the contributions provided by all of the bonds attached to the CH_2 group as well as the contribution due to the C–C bond opposite the CH_2 carbon move downfield. The changes in the bond contributions for the paramagnetic term of the component perpendicular to the local CCC plane are as follows: CH bond 14.5 ppm, neighboring C–C bond 33.0 ppm, and opposite C–C bond 46.7 ppm. Therefore, in this class of molecules, no single factor can be identified as the dominant effect responsible for the large shift, at least by this method of calculation.

A comparison of the CH_2 carbon of cyclopropane, the CH carbon of bicyclobutane and the quarternary carbon of [1.1.1]propellane is difficult due to their quite different bonding environment. While the shift is once again downfield, the changes are smaller than those among the CH_2 carbons. In bicyclobutane the component that lies nearly along the central C–C bond is the furthest downfield as is the component along the central C–C bond in [1.1.1]propellane. The changes in the assignment of the shielding values to the principal axis system for the CH_2 carbon of propellane between different basis sets may be associated with the unusual bonding situation in this compound. While the results for the orientation of the principal axis system are consistent between similar basis sets, i.e. basis sets I and II agree and bases III and IV agree, the significant differences seen between II and III indicate the need for polarization functions for this molecule. Previous work on less unusual molecules [10, 28] had indicated that the relative ordering of shifts and their orientation is quite independent of basis set size. Furthermore, in cases where the orientation of the principal axis system is known either from dipolar or single crystal studies, the calculations had reproduced the experimental findings [28] even with the basis set II.

Acknowledgements. This work was supported by National Science Foundation Grant CHE-8310109. The authors gratefully acknowledge the computer center of the University of Bochum for the use of the CYBER 205.

References

1. Wiberg, K. B.: J. Am. Chem. Soc. **105**, 1227 (1983)
2. Jackson, J. E., Allen, L. C.: J. Am. Chem. Soc. **106**, 591 (1984)
3. Newton, M. D., Schulman, J. M.: J. Am. Chem. Soc. **94**, 773 (1972)
4. Stohrer, W. D., Hoffmann, R.: J. Am. Chem. Soc. **94**, 779 (1972)
5. Wiberg, K. B.: Acc. Chem. Res. **17**, 379 (1984)
6. Wiberg, K. B., Dailey, W. P., Walker, F. H., Cunningham, W., Waddell, S. T., Crocker, L., Newton, M.: J. Am. Chem. Soc., in press
7. Zilm, K. W., Beller, A. J., Grant, D. M., Michl, J., Chou, T. C., Allred, E. L.: J. Am. Chem. Soc. **103**, 2119 (1981)
8. Christl, M.: Chem. Ber. **108**, 2781 (1975)
9. Wiberg, K. B., Walker, F. H.: J. Am. Chem. Soc. **104**, 5239 (1982)
10. Beeler, A. J., Orendt, A. M., Grant, D. M., Cutts, P. W., Michl, J., Zilm, K. W., Downing, J. W., Facelli, J. C., Schindler, M. S., Kutzelnigg, W.: J. Am. Chem. Soc. **106**, 7672 (1984)
11. Wiberg, K. B., Lampman, G. M.: Tet. Let. 2173 (1963)
12. Zilm, K. W., Conlin, R. T., Grant, D. M., Michl, J.: J. Am. Chem. Soc. **102**, 6672 (1980)
13. Mehring, M.: NMR **11**, 1 (1976)
14. Kutzelnigg, W.: Isr. J. Chem. **19**, 193 (1980)
15. Shindler, M., Kutzelnigg, W.: J. Chem. Phys. **76**, 1919 (1982)
16. Schindler, M., Kutzelnigg, W.: J. Am. Chem. Soc. **105**, 1360 (1983)
17. Schindler, M., Kutzelnigg, W.: Mol. Phys. **48**, 781 (1983)

18. Huzinaga, S.: Approximate Atomic Wave Functions. Edmonton, Alberta: University of Alberta, Edmonton, Alberta 1971
19. Harmony, M. D.: J. Phys. Chem. Ref. Data **8**, 3 (1979)
20. Cox, K. W., Harmony, M. D., Nelson, G., Wiberg, K. B.: J. Chem. Phys. **50**, 1976 (1969)
21. Jackowski, K., Raynes, W. T.: Mol. Phys. **34**, 465 (1977)
22. Lazzeretti, P., Rossi, E., Zanasi, R.: J. Am. Chem. Soc. **105**, 12 (1983)
23. Komornicki, A., Pauzat, F., Ellinger, Y.: J. Phys. Chem. **87**, 3847 (1983)
24. Binkley, J. S., Pople, J. A., Hehre, W. J.: Chem. Phys. Lett. **36**, 1 (1975)
25. Buckingham, A. D., Malm, S. M.: Mol. Phys. **22**, 1127 (1971)
26. Zilm, K. W., Grant, D. M.: J. Am. Chem. Soc. **103**, 2913 (1981)
27. Linder, M., Hohener, A., Ernst, R. R.: J. Chem. Phys. **73**, 4959 (1980)
28. Facelli, J. C., Grant, D. M. and Michl, J.: Unpublished results