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Ab initio calculations of the NMR spectra of [1.1.1]propellane and bicyclo[1.1.1]pentane

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New high-level *ab initio* values of all the NMR shielding and spin–spin coupling constants in [1.1.1]propellane and bicyclo[1.1.1]pentane are obtained and compared with previous theoretical results and available experimental data. Electron correlation effects are taken into account and large basis sets suitable for NMR studies are applied. The results for the shielding constants depend primarily on the basis set, while the spin–spin coupling constants, in particular for the carbon–carbon coupling, are very sensitive to electron correlation effects. The computed NMR parameters agree well with the known experimental values, with the exception of the bridgehead–bridgehead carbon coupling constant in [1.1.1]propellane. Our best estimates of this constant differ from the experimental value for a substituted [1.1.1]propellane, and possible explanations of this discrepancy are discussed.

I. Introduction

[1.1.1]Propellane represents an ultimate example of a known molecule having carbon atoms with the inverted configuration, strongly departing from the tetrahedral geometry.[1–4] The unusual structure (Fig. 1) and remarkable stability of this molecule have attracted a lot of attention from both experimental[5–10] and theoretical chemists.[9,11–15] Since its synthesis in 1983[5] the properties of [1.1.1]propellane have been studied by various physicochemical methods, see for example ref. 6–10.

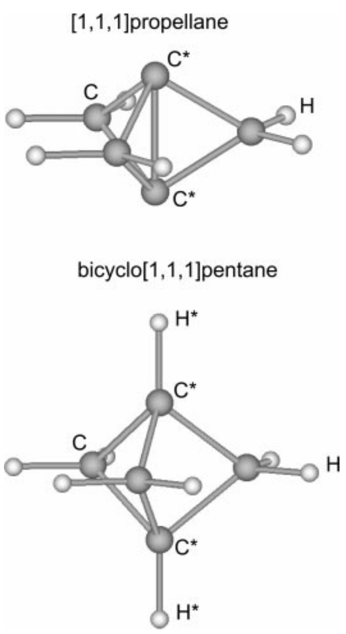

Fig. 1 The geometry and labelling of atoms in [1.1.1]propellane and bicyclo[1.1.1]pentane.

The existence and role of the bridgehead–bridgehead bond in propellanes has been discussed in a number of theoretical papers,[11–15] mainly in the 1980s. A maximum in the bond path for the central C*C* bond has been found by Wiberg *et al.*,[14,15] who thus concluded that a bridgehead–bridgehead bond exists in each of the propellanes. An experimental indication of the role of the central bond in [1.1.1]propellane could be obtained from studies of NMR chemical shifts and especially from coupling constants for the molecule in question by comparing their values with those in bicyclo[1.1.1]pentane which can be regarded as hydrogenated [1.1.1]propellane (see Fig. 1), and lacks the central bridgehead–bridgehead bond.

The complete set of the components of the ^{13}C shielding tensor is known from experiment[16,17] for both molecules. In contrast to that, the available experimental data for the spin–spin coupling constants in [1.1.1]propellane[2,9,18] and bicyclo[1.1.1]pentane[2,19] are incomplete. The spin–spin coupling constant between the bridgehead carbons in propellane, the most revealing parameter, cannot be obtained from standard experimental spectra since these nuclei are magnetically equivalent. On the other hand, in bicyclo[1.1.1]pentane the bridgehead carbon and hydrogen nuclei form an AA′XX′ system and in principle $J(C^*C^*)$ can be measured. However, to our knowledge the experimental values for this coupling in both molecules were obtained only for alkyl-substituted derivatives.[20]

Accurate values of the NMR parameters can be obtained from *ab initio* calculations. However, up to now the NMR parameters in [1.1.1]propellane and bicyclo[1.1.1]pentane

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have been calculated only at a low level of theory: the spin–spin coupling constants at the random-phase approximation (RPA)[19,21] or similar[22] level and the NMR shielding constants at the self-consistent field (SCF) level.[16,17,23–25] In addition, relatively small basis sets have been used in these studies. Current *ab initio* calculations of the NMR shieldings and also of more demanding spin–spin coupling constants have reached the stage when semi-quantitative results can be obtained,[26] even for relatively large systems like the title molecules. Therefore, we have carried out high-level correlated *ab initio* calculations of the NMR shielding constants and the coupling constants to get an insight into the differences between the NMR parameters of these two molecules, since such differences are mainly due to the nonstandard bonding in propellane. Our calculations are more extensive than previous theoretical studies of the NMR parameters in [1.1.1]propellane and bicyclo[1.1.1]pentane; for many of these parameters there are no previous *ab initio* results or only the SCF approximation has been used.

II. Computational details

The geometric structures of [1.1.1]propellane and bicyclo[1.1.1]pentane have been optimized using the correlation-consistent cc-pVTZ basis set[27] at the MP2 level. The optimization has been performed within the D_{3h} symmetry. Test calculations without the symmetry restriction have led to the same results.

The NMR shielding constants and the spin–spin coupling constants have been calculated by means of the linear response MCSCF method.[28–30] For NMR shielding constants, the SCF and MP2[31,32] results are reported in addition to the MCSCF values, while for the coupling constants we report also the CCSD values. The analysis of the CI coefficients in the MCSCF wavefunction reveals that the main difference between [1.1.1]propellane and bicyclo[1.1.1]pentane is, predictably, the relatively large (≈ -0.08) coefficient of the second determinant in [1.1.1]propellane. An advantage of using the MCSCF approach is that the double excitation to the C*C* antibonding orbital is well described in the reference wavefunction, hence the response properties of a partly biradical, two-determinant [1.1.1]propellane and single-determinant bicyclo[1.1.1]pentane are treated at the same level.

Three restricted active space self-consistent field (RASSCF) functions, analogous for both molecules, denoted RAS-I, RAS-II and RAS-III, have been used for [1.1.1]propellane and bicyclo[1.1.1]pentane. We describe the division of the orbitals into the inactive, RAS2, and RAS3 space (RAS1 is empty) specifying the numbers of orbitals in A_1', A_2', E', A_2'', A_1'', and E'' representations of D_{3h} symmetry. The (2 0 1 1 0 0) carbon 1s core orbitals are kept inactive for both molecules. The RAS2 space consists of (3 1 3 1 0 1) orbitals for [1.1.1]propellane and (3 1 3 2 0 1) for bicyclo[1.1.1]pentane. The RAS-I, RAS-II and RAS-III wavefunctions differ only in the size of the RAS3 subspace. In RAS-I, (2 1 3 2 0 1) orbitals are included in the RAS3 space for [1.1.1]propellane and (3 1 3 2 0 1) orbitals for bicyclo[1.1.1]pentane. In the RAS-II wavefunctions, the RAS3 size is (5 1 6 3 1 3) for both molecules, while in RAS-III wavefunctions it is (6 2 8 5 1 4) for [1.1.1]propellane and (7 2 8 4 1 5) for bicyclo[1.1.1]pentane. A maximum of two electrons are allowed to be excited to the RAS3 space in all the approximations. The employed RASSCF wavefunctions are designed to provide results of uniform quality for both molecules. The choice of the active orbitals in RAS3 spaces has been based on the MP2 occupation numbers.

To test the accuracy of these calculations, we have also used for each molecule different wavefunctions. These included a wavefunction with a RAS3 space intermediate between RAS-I and RAS-II, a wavefunction with core orbitals active and a wavefunction with 4 (instead of 2) electrons allowed to be excited into the RAS3 space. Since the results do not differ significantly from those for the wavefunctions described above we shall not discuss them further.

The calculations of the spin–spin coupling constants and the NMR shielding constants have been carried out in the HIII basis set,[33] derived from the basis sets of Huzinaga[34,35] and successfully used in numerous previous calculations of the NMR parameters (see *e.g.* ref. 26 and 36 and references therein). This basis, consisting of [11s7p2d/7s6p2d] functions for C and [6s2p/4s2p] for H atom, yields a total of 235 CGTOs for C_5H_6 and 255 CGTOs for C_5H_8. It differs from standard bases as it includes relatively more tight functions (particularly of s symmetry), thus, although not very large, the HIII basis describes well the neighbourhood of the nucleus, the region of the molecule relevant for the calculation of NMR parameters. The spin–spin coupling constants have been additionally calculated using the HII basis set, similar to HIII, but smaller. The GIAO[37–39] orbitals have been used in the calculations of the NMR shielding constants.

The linear response MCSCF calculations have been carried out by means of the Dalton[40] program. The GAUSSIAN98 package[41] has been used for the SCF, DFT and MP2 calculations. The indirect spin–spin coupling constants have been calculated in addition at the CCSD level as unrelaxed second derivatives of the CCSD energy,[42] using the program based on Aces II[43] (for a description of CCSD second derivatives in the UHF framework, see ref. 44). The same method has been used in other recent spin–spin coupling calculations in ref. 45 and 46.

In this manuscript we do not discuss the individual tensor components of the coupling tensors, as there are no experimental data for comparison. The calculated spin–spin coupling constants are reported even when the nuclei are magnetically equivalent and the coupling does not affect standard NMR spectra.

III. Results

We first compare for both molecules the optimized geometries with the experimental data. Accurate geometries are needed for a reliable calculation of the NMR parameters. In the next section we analyze the isotropic shielding and, in addition, discuss those individual shielding tensor components for which experimental data are available. The spin–spin coupling constants are described in the last section. We concentrate on the accuracy of the calculations and discuss the effects complicating the comparison of theoretical and experimental results.

A. The geometric structure

The structures of [1.1.1]propellane and bicyclo[1.1.1]pentane are visualised in Fig. 1. The geometric structure of [1.1.1]propellane and bicyclo[1.1.1]pentane cages is fully described by a set of C*C* (bridgehead carbon–bridgehead carbon) and CC* (bridgehead carbon–bridge carbon) distances. An inspection of the results of the calculations indicates that the calculated value of the C*C* distance in [1.1.1]propellane (159.7 pm) is in excellent agreement with the corresponding experimental data (ranging from 159.3 to 160.5 pm (ref. 2)). Our calculated CC* bond length (151.7 pm) is somewhat smaller than most of the reported experimental values: 152.5 ± 0.2 from electron diffraction (ED) measurements,[7] 152.2 ± 0.2 from IR and Raman spectroscopy,[8] and 151.2–155.5 pm from X-ray measurements.[6] The calculated CC* and C*C* distances in bicyclo[1.1.1]pentane (187.5 and 155.0 pm) are close to the respective experimental ED values 187.4 ± 4 and 155.7 ± 2 pm.[47] In principle, our calculations of the geometric structure provide the most accurate theoretical data since the previous theoretical studies have been carried out at only the SCF[19,22] or DFT[10,25] levels with smaller basis sets.

B. The NMR shielding constants

Isotropic ^1H and ^{13}C shielding constants for [1.1.1]propellane and bicyclo[1.1.1]pentane obtained by means of the SCF, MP2, and MCSCF methods are summarized in Table 1. Table 2 contains the calculated individual components of the carbon shielding constants, compared with the experimental data and previous *ab initio* values.[16,17,23]

To convert the experimental chemical shift data to absolute shielding constants we have used the recently calculated values for the shielding in TMS: 199.0 ppm for the carbon atom[48] and 31.59 ppm for the hydrogen atom.[49] We have also converted back to the absolute shielding scale some of the literature *ab initio* chemical shift values quoted below.

In the case of the ^{13}C shielding constants, the RASSCF results seem to be in better agreement with experimental values (in particular with those of ref. 9 for [1.1.1]propellane and ref. 17 and 23 for bicyclo[1.1.1]pentane) than the SCF and MP2 results. However, the correlation effects are not very substantial.

For the propellane ^{13}C shielding constants, the theoretical IGLO-SCF results are essentially in agreement with our values. For bicyclopentane, the IGLO-SCF results of ref. 17 and 23 differ more from our results. Since the correlation effects are rather small, we attribute this to the smaller basis sets used for bicyclo[1.1.1]pentane (this is also supported by significant differences between the small basis I and II and final basis IV IGLO-SCF values for propellane in ref. 16).

In contrast to the ^{13}C shielding constants, the ^1H shielding constants calculated at the MP2 level are apparently in better agreement with the experimental results than the RAS-II ones. However, it should be kept in mind that the comparison between experimental and theoretical shielding constants is impaired by the uncertainty of the TMS reference scale and by the solvent effects.

For completeness, the shielding constants have been calculated also at the DFT level, employing the B3LYP functional as implemented in GAUSSIAN98.[41] The results for the ^{13}C shielding constants (Table 1) differ from the values obtained by other methods and from experiment, therefore we do not discuss them in the following analysis of shielding tensor components. The DFT results for ^1H shielding constants are similar to the MP2 values and relatively close to experiment.

The importance of the sufficiently large basis set for the calculations of the ^{13}C NMR shielding constants is further emphasised when the theoretical (present work and ref. 16, 17 and 23) individual tensor components are compared with the experimental data (Table 2). For [1.1.1]propellane, where the differences between individual tensor components are substantial for both types of carbon atoms, the assignment of the experimental values is straightforward and unambigous. Bicyclo[1.1.1]pentane, however, presents a more difficult problem, since the two components for the methylene carbon atoms are very close to each other.[23] The assignment based on the IGLO-SCF results[23] should, according to our calculations, be modified. The proper assignment of the experimental values is given in Table 2. The components are, in order of magnitude, σ_C, σ_A and σ_B (σ_A and σ_B are similar), not σ_B, σ_C and σ_A as in ref. 23. We base this conclusion on the considerably better agreement of our results with experiment for all the ^{13}C shielding tensor components of bicyclo[1.1.1]pentane. Also the shielding components of the bridgehead carbon nucleus calculated in the present work are considerably closer to experiment than the results from ref. 17, and in this case the assignment does not differ. The main reason for the improvement of our theoretical results over those in ref. 17 and 23 is the larger basis set, since the correlation effects are small.

C. The spin–spin coupling constants

The comparison of the calculated spin–spin coupling constants in [1.1.1]propellane and bicyclo[1.1.1]pentane with the results of previous theoretical studies and the experimental values is presented in Table 3. The RAS-I values are tabulated

Table 1 The comparison of the theoretical and experimental results for the isotropic shielding constants (in ppm)

	[1.1.1]Propellane					Bicyclo[1.1.1]pentane				
	SCF/ HIII	MP2/ HIII	RAS-II/ HIII	Exp.	Other calc.	SCF/ HIII	MP2/ HIII	RAS-II/ HIII	Exp.	Other calc.
C*	196.5	195.8	199.2	194.7[a] 198.0[d]	196.3[a], 177.9[b] 205.3[e]	163.3	159.4	165.0	165.3[c]	185[c], 144.1[b]
C	116.1	118.2	122.1	119.7[a] 124.8[d]	121[a], 100.0[b] 128.4[e]	145.9	140.9	149.0	149.7[f]	168[f], 126.2[b]
H	30.2	29.8	30.1	29.53[d]	29.9[b]	30.5	29.8	30.2	29.75[g]	30.0[b]
H*						30.0	29.4	29.9	29.15[g]	29.5[b]

[a] Experiment in the solid state and IGLO-SCF, ref. 16. [b] B3LYP/HIII, this work. [c] Experiment in the solid state and IGLO-SCF, ref. 17. [d] Ref. 9. [e] GIAO-SCF, ref. 24. [f] Experiment and IGLO-SCF, ref. 23. [g] Ref. 2.

Table 2 The comparison of the theoretical and experimental results for the carbon shielding tensors (in ppm)

	[1.1.1]Propellane					Bicyclo[1.1.1]pentane				
	SCF/ HIII	MP2/ HIII	RAS-II/ HIII	Exp.[a]	Other calc.[a]	SCF/ HIII	MP2/ HIII	RAS-II/ HIII	Exp.	Other calc.
C*										
σ_{iso}	196.5	195.8	199.2	194.7	196.3	163.3	159.4	165.0	165.3[b]	185[b]
$\sigma_{\parallel}$	166.6	162.9	167.9	164	169	183.8	182.8	186.3	182[b]	194[b]
$\sigma_{\perp}$	211.4	212.3	214.9	210	210	153.1	147.6	154.4	157[b]	180[b]
C[c]										
σ_{iso}	116.1	118.2	122.1	119.7	121.0	145.9	140.9	149.0	149.7[d]	168[d]
σ_A	152.9	156.0	157.3	156	156	144.6	140.4	147.2	145[d]	152[d]
σ_B	139.1	135.2	142.9	142	146	137.0	133.7	141.7	143[d]	177[d]
σ_C	56.2	63.4	66.1	61	61	156.1	148.7	158.1	161[d]	174[d]

[a] Experiment in the solid state and IGLO-SCF calculations, ref. 16. [b] Experiment in the solid state and IGLO-SCF calculations, ref. 17. [c] For the methylene carbon atom, the tensor components are: σ_A, bisecting the HCH angle; σ_B, perpendicular to the HCH plane and σ_C, perpendicular to the C*CC* plane. [d] Experiment and IGLO-SCF, ref. 23 (our assignment of axes for the experimental data, see text).

Table 3 The comparison of the theoretical and experimental results for the spin–spin coupling constants (in Hz)[a]

	[1.1.1]Propellane				Bicyclo[1.1.1]pentane			
	RAS-I/HIII	Best results[b]	Exp.[c]	Other calc.	RAS-I/HIII	Best results[b]	Exp.[c,d]	Other calc.[d]
J(C*C*)	42.93	42.89		1.59[e]	−33.64	−35.09		−33.84
		(21.84)	*0.6*			(−28.41)	*−25.1*	−25.76[e]
^1J(C*C)	20.28	17.15	9.9[f]	—	37.92	35.82	25.1	52.28
		(10.55)	*10.2*			(26.48)	*25.3*	
^2J(CC)	−2.90	−3.27	—	—	−9.42	−9.47		−19.44
		(−0.62)				(−5.54)	*−5.2*	
^1J(C*H*)					160.12	165.20	167.8, 164	154.5
^1J(CH)	163.49	162.84	165,[g] 163.7[f]		144.91	144.13	144.5, 144	161.17
^3J(C*H*)					12.52	12.1	10.0[h]	11.63[h]
^2J(CH*)					−1.33	−1.27	≈0[i]	−3.50
^3J(C*H)	−3.25	−2.79	—	—	−5.86	−5.41	3	−9.01
t − ^3J(CH)	15.45	15.73	—	—	16.1	16.36	15.5	17.29
c − ^3J(CH)	5.16	5.15	—	—	7.74	7.70	7.8	9.27
^3J(HH*)					0.33	0.28	≈0[i]	0.55
^4J(H*H*)					16.35	16.64	18.2, 18	19.52
^2J(HH)	−6.42	−5.92	—	—	−6.65	−5.96	—	−13.82
t − ^4J(HH)	0.20	0.32	—	—	−0.07	0.02	≈0[i]	−0.75
c − ^4J(HH)	−0.33	−0.29	—	—	−0.54	−0.50	≈0[i]	−0.73
W − ^4J(HH)	5.58	5.87	—	—	7.88	8.30	9.6, 10	9.14

[a] Following ref. 19 we denote the different ^4J(HH) couplings as transoid, cisoid and W-type, called in the table t − ^4J(HH), c − ^4J(HH) and W − ^4J(HH). [b] Obtained by adding RAS-II or CCSD (in parentheses) values of the dominant FC term and RAS-I values of the other contributions. For the description of RASSCF wavefunctions, see text. [c] In italics: ref. 20, average of the values for the alkyl-substituted compounds (see text), minus signs attributed according to the computed values. [d] Ref. 19 unless otherwise stated. [e] Ref. 22. [f] Ref. 18. [g] Ref. 9. [h] The same values are also discussed in ref. 21. [i] Ref. 19—too small to be observed.

together with our best estimates, based on the CCSD calculations for carbon–carbon coupling constants and RAS-II calculations for the other constants. We compare our results for the carbon–carbon coupling constants in [1.1.1]propellane with the averaged constants for the 2-methyl-butyl-substituted propellane, the experimental data for the 1-methyl-propyl-derivative were very similar.[20] For bicyclo[1.1.1]pentane, the corresponding constants were reported for 2-methyl-pentyl- as the substituent replacing a methylene hydrogen atom.[20]

The RAS-I results are generally close to the experimental data for both molecules and the extension of the active space to RAS-II brings the calculated couplings into even better agreement with experiment. The carbon–carbon coupling constants are an exception, and the more accurate CCSD values of these constants are discussed in detail below. The comparison of the coupling constants in bicyclo[1.1.1]pentane calculated by means of our MCSCF wavefunction, the SCF-level results of Lazzeretti *et al.*[19] and the experimental data favours our results. This is understandable, since the coupling constants in ref. 19 were obtained within the SCF approximation, which significantly affects the quality of the triplet FC and SD contributions, even for saturated hydrocarbons. Also the basis sets used in ref. 19 are smaller than those employed in the present study.

For a more thorough analysis of the correlation effects on the carbon–carbon coupling constants, we performed also CCSD and RAS-III calculations of the most important Fermi contact contributions. We have used the HII IGLO basis set,[33] smaller than HIII, but leading to very similar results at the RAS-I level. The results are summarized in Table 4. We have verified that some extensions of the basis set within the CCSD approach do not affect the results. Using the HIII basis for the C* atoms in both molecules or for all the carbon atoms in propellane we obtain results which differ by less than 1.5 Hz from the tabulated CCSD values. For the carbon–carbon coupling constants in bicyclo[1.1.1]pentane all the CCSD results are in good agreement with the experimental data. Also the FC contribution to ^1J(C*C) in [1.1.1]propellane obtained at the CCSD level leads to a far better agreement with the experimental value than the RASSCF results. The difference between the computed and experimental values of J(C*C*) for [1.1.1]propellane is reduced in comparison to the RASSCF values, but still remains significant. It may be partly due to the worse performance of the single-reference CCSD approach for [1.1.1]propellane and partly (see below) due to the difficulties in the comparison of theoretical and experimental values.

The CCSD value of the FC contribution to ^1J(CH) is only 149.08 Hz, much smaller than the experimental and RASSCF results. The other results do not differ significantly. The same trends are observed for bicyclo[1.1.1]pentane: CCSD performs better (in terms of agreement with experiment) for the carbon–carbon couplings, while RASSCF results are systematically superior for the carbon–proton couplings.

The CCSD results indicate that our RAS-II function does not describe all the required dynamic correlation effects. Accordingly, we attempted to improve the calculated values of carbon–carbon couplings, in particular J(C*C*), by extending the RASSCF wavefunction (to RAS-III) or allowing more excitations into the RAS3 space (4 electrons instead of 2). The

Table 4 The FC contributions to the carbon–carbon spin–spin coupling constants (in Hz)

	[1.1.1]Propellane				Bicyclo[1.1.1]pentane			
	RAS-I/HIII	RAS-I/HII	RAS-III/HII	CCSD/HII	RAS-I/HIII	RAS-I/HII	RAS-III/HII	CCSD/HII
J(C*C*)	39.45	39.34	34.63	18.36	−33.95	−35.21	−36.09	−28.73
^1J(C*C)	22.84	23.81	19.77	13.12	37.19	38.70	35.30	25.75
^2J(CC)	−2.65	−2.58	−2.67	−0.37	−9.32	−9.66	−9.43	−5.44

former change led to a lowering of the $J(C^*C^*)$ value by 4.5 Hz (see Table 4), while the latter caused a lowering by 5.2 Hz. These trends are in the right direction, but the convergence is too slow to make further calculations of this type practical. It seems that even the largest used RASSCF active spaces do not encompass the orbitals required for a proper description of the carbon–carbon couplings, and for these constants the CCSD values are more reliable. Apparently, for a reliable calculation of the $J(C^*C^*)$ spin–spin coupling constant in [1.1.1]propellane one needs a multiconfigurational approach and an appropriate treatment of dynamic correlation effects. Therefore, the agreement of the results obtained in ref. 22 with experiment appears to be fortuitous and may be due to a cancellation of errors (for example, a rather small basis set had been used).

Usually, simultaneous convergence of the spin–spin coupling constants in a molecule to the correct results is observed when the level of the calculations is improved (see *e.g.* ref. 50 and 51). Considering the good agreement of all the other CCSD carbon–carbon constants in both bicyclo[1.1.1]pentane and [1.1.1]propellane with experiment we expect the computed $J(C^*C^*)$ coupling in [1.1.1]propellane to be of similar quality. Although a very accurate calculation of this parameter may require a better description of both static and dynamic correlation effects, it appears unlikely that the difference between the calculated $J(C^*C^*)$ in [1.1.1]propellane and the experimental results for alkyl-substituted derivatives can be fully explained by the approximations we have made in the calculations.

The calculated and measured $J(C^*C^*)$ values differ partially due to the substituent and solvent effects present in experiment. The one-bond carbon–carbon coupling constants are normally not very sensitive to the substituent effects. However, the unusual bridgehead–bridgehead coupling in [1.1.1]propellane may be an exception, with substituent effects comparable to those in alkynes.[52] We note that the substituents used are asymmetric and (for two out of three compounds studied) longer than propellane or bicyclopentane itself. The solvent effect may also be substantial. It should be kept in mind that there are two contributions to the solvent effect which have to be considered: a direct effect on NMR properties, and an indirect effect, due to the change of molecular geometry resulting from solute–solvent interactions. It has been noticed that this geometry relaxation effect may be important for the spin–spin coupling constants,[53] and we believe this may also be the case for propellane, because of its partly biradical character.

We have not discussed the individual contributions to the spin–spin coupling constants in [1.1.1]propellane and bicyclo[1.1.1]pentane in detail. All the spin–spin coupling constants are dominated by their Fermi contact terms (for the H–H coupling constants, the large PSO and DSO terms almost cancel, as for many other molecules, see *e.g.* ref. 50). A relatively large spin–dipole contribution is present only in the $J(C^*C^*)$ coupling constants in [1.1.1]propellane. The dominance of the FC term justifies the neglect of the other contributions in the calculations employing the large RAS-II and RAS-III active spaces, or the CCSD method.

IV. Conclusions

The shielding and spin–spin coupling constants have been calculated for [1.1.1]propellane and bicyclo[1.1.1]pentane at the MP2, MCSCF and CCSD levels. The MCSCF method makes it possible to treat with uniform accuracy bicyclo[1.1.1]pentane with its essentially single-reference character and [1.1.1]propellane with large static correlation effects.

The geometric structures obtained at the MP2 level with relatively large basis sets should, in principle, be very accurate, and our results are indeed bracketed by the experimental data. The optimized molecular geometries used in the calculations of NMR parameters represent well the structures of isolated molecules in the lowest rovibrational states.

The ^{13}C shielding constants obtained at the RASSCF level are in excellent agreement with experiment. The accuracy of our calculations of the shielding constants enabled us to reassign the individual components of methylene ^{13}C shielding tensor in bicyclo[1.1.1]pentane, obtained from the solid state NMR experiment. The differences between our theoretical values and experimental data are slightly larger for the ^1H shielding constants. Although these comparisons are tainted by uncertainty of the TMS reference values, all the relative chemical shifts of the carbon nuclei are undoubtedly well reproduced.

The proton–carbon and proton–proton spin–spin coupling constants calculated at the MCSCF level are also in good agreement with experiment, in particular the $^1J(CH)$ couplings in both molecules. For the carbon–carbon coupling constants the convergence with the extension of the MCSCF active space is too slow. Thus, the experimental carbon–carbon coupling constants are reproduced much better by the CCSD calculations. Only for the $J(C^*C^*)$ coupling constant in [1.1.1]propellane does even the CCSD result remain significantly larger than the corresponding experimental values for alkyl-substituted derivatives. It appears that the measured $J(C^*C^*)$ coupling constant is modified by large solvent or substituent effects, contributing to the discrepancy between experiment and theory. In such cases, when direct experimental measurements are not possible or difficult, systematic theoretical studies are particularly valuable. Undoubtedly, further experimental measurements of the coupling constants of the $J(C^*C^*)$ type would also be of interest.

Finally, we observe clearly a large change in $J(C^*C^*)$ from bicyclo[1.1.1]pentane to [1.1.1]propellane, which indicates a very different character of the coupling path in these two molecules. This change is of the same order of magnitude as the carbon–carbon coupling constant in ethane, confirming the role of the bridgehead–bridgehead bond in [1.1.1]propellane.

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