

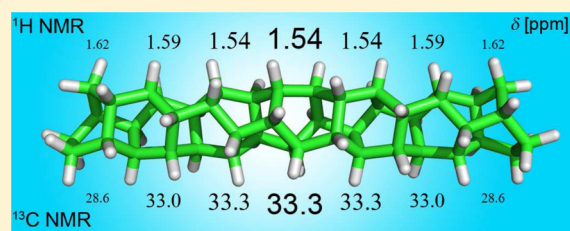
Calculated Nuclear Magnetic Resonance Spectra of Polytwistane and Related Hydrocarbon Nanorods

Boris Maryasin, Martin Olbrich, Dirk Trauner,* and Christian Ochsenfeld*

Department of Chemistry, University of Munich (LMU), and Munich Center for Integrated Protein Science (CIPSM), Butenandtstrasse 5-13, D-81377 Munich, Germany

S Supporting Information

ABSTRACT: Polytwistane is an intriguing hydrocarbon nanorod that has not been experimentally realized to date. To facilitate its identification in complex reaction mixtures, the ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra of idealized polytwistane were calculated using two distinct quantum chemical approaches. In addition, the NMR spectra of related hydrocarbon nanorods were determined. On the basis of these data, we speculate whether polytwistane and its congeners correspond to a crystalline one-dimensional sp^3 carbon nanomaterial formed by high-pressure solid-state polymerization of benzene.



1. INTRODUCTION

Polytwistane (Figure 1) was recently proposed as a chiral polymer with intriguing structural features, which were studied computationally by optimizing the geometry at the B3LYP/6-31G(d) level of theory and by rigorous topological analysis.¹ It displays hydrogen atoms and sp^3 -hybridized carbons that all possess the same chemical environment. The helical polymer is an isomer of polyacetylene (C_2H_2)_n and has an inner diameter of 2.6 Å. The principal viability of polytwistane was demonstrated computationally using homodesmotic equations,² which showed that its formation from acetylene is highly exothermic.

So far, attempts to synthesize polytwistane (1) through polymerization of acetylene have not been successful.³ Recently, it has been suggested that polytwistane-like structures are present in a crystalline one-dimensional sp^3 carbon nanomaterial formed by high-pressure solid-state polymerization of benzene.⁴ Indeed, it is conceivable that polytwistane (1) could be formed from acetylene or its oligomers, such as benzene or cyclooctatetraene, under extreme conditions.

Because of the high symmetry of idealized polytwistane (1), both its ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra should consist of a single peak. In this work, we calculate spectra of oligotwistanes of different lengths and demonstrate that these converge onto spectra that correspond to idealized polytwistane (1). Thus, our calculations are expected to facilitate the identification of these materials in actual samples.

Quantum chemical calculations of NMR spectra can be performed today at different levels of theory ranging from Hartree–Fock (HF)^{5–7} or density functional theory (DFT)⁸ to wave function-based correlation methods like, e.g., Møller–Plesset second-order perturbation theory (MP2)^{9–11} and coupled-cluster (CC) methods.^{12,13} Unfortunately, the corre-

lated levels are applicable only for relatively small systems. Therefore, for large molecules such as polytwistane nanorods (1) only calculations at either the HF or DFT level are accessible using modern linear-scaling NMR methods.^{14,15}

Recent benchmarking studies for ^{13}C and ^1H NMR shift calculations, such as those by, e.g., Lodewyk et al.,¹⁶ Teale et al.,¹⁷ and Flaig et al.,¹⁸ show that unfortunately no general and at the same time economical computational recipe exists. The authors use very different quantum chemical methods, basis sets, and reference systems. These studies have one similar feature: the calculations were performed for the sets of “standard” small organic molecules. The polytwistane (1) system is an unclassical one; i.e., the polycyclic nanotube structure is clearly different from all of the systems studied before. On the other hand, there are no experimental data available for the NMR chemical shifts of polytwistane (1). As a result, it is necessary to identify a computational scheme that is suitable for the reliable calculation of the NMR chemical shifts of polytwistane (1). We compare here the performance of a series of DFT functionals with the *ab initio* methods MP2 and CCSD. We also compare different computational approaches to obtain the chemical shifts from the calculated data, namely a linear regression scheme relying on experimental data and the quantum chemical nonempirical approaches.

2. COMPUTATIONAL DETAILS

All NMR calculations were performed using gauge-including atomic orbitals (GIAO).^{5,6,19} The applied *ab initio* methods for calculating NMR data are CCSD(T),¹³ CCSD,¹² MP2,^{9–11} and HF.^{5–7} The RI-MP2^{20,21} method was applied for geometry optimizations. The selection of DFT functionals includes

Received: December 19, 2014

Published: February 25, 2015



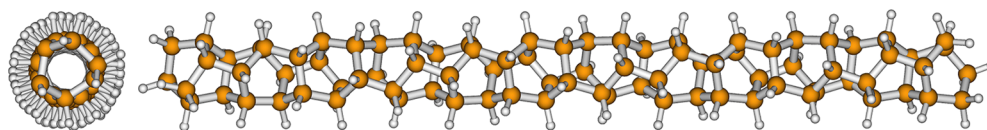


Figure 1. Top (left) and side (right) views of a $C_{86}H_{92}$ fragment of polytwistane (1) optimized at the PBE0-D3/def2-TZVP level of theory.

hybrid GGA functionals PBE0²² (also in combination with the DFT-D3²³ dispersion correction for geometry optimizations), B97-2,²⁴ and B3LYP^{25,26} and pure GGA functional KT2.²⁷ Basis sets def2-SVP, def2-TZVP,²⁸ and pcS-1²⁹ were chosen. For geometry optimizations and MP2 chemical shift calculations, the Turbomole 6.3.1 program package³⁰ was used. The CCSD¹² and CCSD(T)¹³ NMR calculations were performed with CFOUR.³¹ The NMR calculations at different DFT levels were performed with a development version of the Q-Chem program package³² and the newly developed QM package FermiONs+.³³ For the calculations according to the linear regression scheme developed by Lodewyk et al.¹⁶ at the B3LYP/6-31+G(d,p)-CPCM//B3LYP/6-31G(d) level of theory, Gaussian03 was used.³⁴

3. CALCULATION OF THE NMR CHEMICAL SHIFTS OF IDEALIZED POLYTWISTANE

3.1. A Linear Regression Approach. As a first approach, we followed a method developed by Lodewyk et al.,¹⁶ using a linear regression for error reduction in the generation of NMR chemical shifts from calculated isotropic shifts. Validation experiments showed that the polycyclic nature of polytwistane (1) and oligotwistanes demands reparametrization of the reported scaling factors. As a consequence, NMR spectra of a range of bi- to hexacyclic compounds, synthesized in our laboratory, were calculated (in accordance with the suggestion of Lodewyk et al.¹⁶) at the B3LYP/6-31+G(d,p)-CPCM//B3LYP/6-31G(d) level of theory and used to establish new scaling factors specific for these types of systems. Table 1 presents a comparison of the reported and new scaling factors.

Table 1. Reported Values of Slopes and Intercepts for the B3LYP/6-31+G(d,p)-CPCM-SCRF//B3LYP/6-31G(d) Computational Method Compared to Values Obtained from a Test Set of Bi- to Pentacyclic Compounds

	¹³ C NMR		¹ H NMR	
	slope	intercept	slope	intercept
generic test set ¹⁶	−1.0472	31.6874	−0.9600	190.0155
polycyclic test set	−1.0787	31.7710	−0.9635	187.150

As a validation for these linear regression values, the computational and experimental data for tritwistane³ were compared, resulting in a standard deviation of 0.06 ppm for its ¹H NMR and 1.43 ppm for its ¹³C NMR chemical shifts. Subsequently, the computational data for oligotwistanes $C_{20}H_{26}$, $C_{26}H_{32}$, $C_{32}H_{38}$, $C_{44}H_{50}$, and $C_{46}H_{52}$ were evaluated using the new linear regression data. The convergence of the methine chemical shifts is only observed for oligotwistanes with more than 32 carbon atoms, reflecting the influence of the terminal methylenes. The results for $C_{46}H_{52}$ (Figures 2 and 3) show convergence of the chemical shifts in ¹H NMR to 1.85 ppm and in ¹³C NMR to 35.5 ppm. Assuming that the chemical environment of the methines should not change significantly in going to the ideal polymer, these chemical shifts represent our

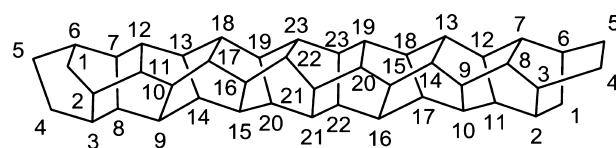


Figure 2. Structure and numbering of $C_{46}H_{52}$ oligotwistane.

first estimate for the values expected for infinite polytwistane (1).

3.2. A Nonempirical Approach. As an alternative, a more elaborate nonempirical quantum chemical approach was employed, using recently developed linear-scaling NMR methods.^{14,15} In this approach, the chemical shift of the methine in twistane (Figure 4) relative to tetramethylsilane was used as the intermediate computational reference. This approach of an intermediate reference method has been found to provide reliable results.^{35,36} The errors in NMR shift calculations can be significantly decreased, as the shifts of the probed structure are computed with respect to a closely related structure (intermediate reference). According to this approach, the total shift with respect to TMS ($\delta_{TMS-sample}^{high/low}$) is determined as the sum of a highly accurate theoretical (or possibly also experimental) shift value ($\delta_{TMS-Int.ref.}^{high}$) for the intermediate reference and an incremental shift ($\delta_{Int.ref-sample}^{low}$) computed at a lower level:

$$\delta_{TMS-sample}^{high/low} = \underbrace{\delta_{TMS-Int.ref.}^{high}}_{\sigma_{TMS}^{high} - \sigma_{Int.ref.}^{high}} + \underbrace{\delta_{Int.ref-sample}^{low}}_{\sigma_{Int.ref.}^{low} - \sigma_{sample}^{low}}$$

Table 2 lists chemical shifts of twistane calculated at different levels of theory relative to TMS and compares the computational data with the experiment. The CCSD(T)/pcS-1 and the experimental shifts were chosen as the intermediate reference for the following calculations for tritwistane and larger oligotwistanes. Because of the large computational effort, it is not practical to use the larger basis sets pcS-2 and pcS-3 with coupled-cluster methods even for the smallest twistane. Relying on MP2 and B97-2 results and assuming the similar basis set convergence behavior for different methods, one could estimate an error of 2.7 ppm for ¹³C NMR and 0.16 ppm for ¹H NMR because of the basis set size. However, the intermediate reference method employed in this work leads to a significant error cancellation, because the errors for the larger members of the twistane family and the twistane (the intermediate reference) are similar in magnitude (for more details, see the Supporting Information). Thus, the use of the pcS-1 basis set seems to be a very good compromise, as compared to the very expensive pcS-2 or pcS-3 calculations for the large oligotwistanes. One has to note also that additional deviations of the calculated values from the experiment can be connected to, e.g., vibrational effects, which are neglected in our calculations.

As the model system for the following benchmark and validation calculations, tritwistane was used, for which experimental data are available from earlier work in our

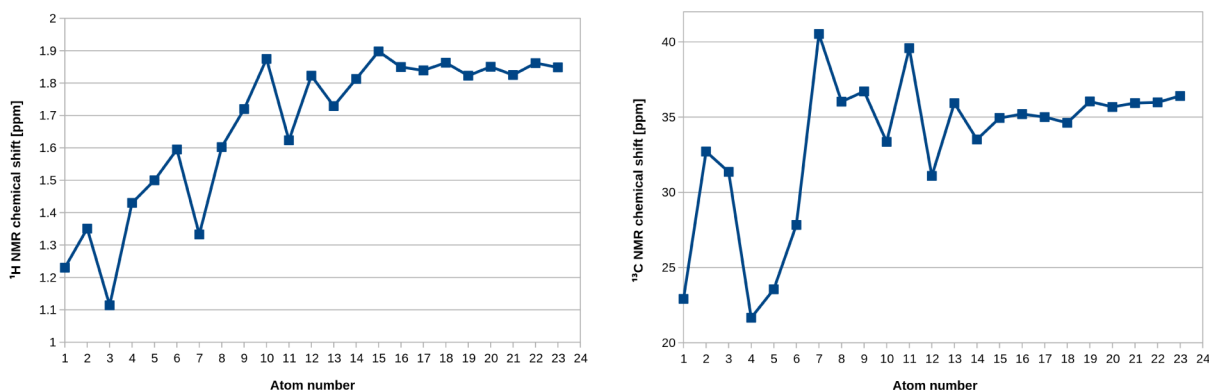


Figure 3. Calculated ^1H and ^{13}C NMR chemical shifts corresponding to the atom number specified in $\text{C}_{46}\text{H}_{52}$ oligotwistane (Figure 2). The shifts are obtained at the B3LYP/6-31+G(d,p)-CPCM//B3LYP/6-31G(d) level of theory by applying the linear regression approach.

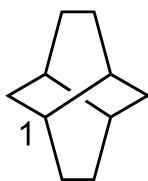


Figure 4. Structure of twistane.

Table 2. Calculated and Experimental ^{13}C and ^1H NMR Chemical Shifts of Twistane

	chemical shift (ppm)	
	C1	C1-H
experiment ³⁷	28.4	1.33–1.63
CCSD(T)/def2-SVP	26.2	1.32
CCSD(T)/pcS-1	29.4	1.43
CCSD/def2-SVP	25.5	1.27
CCSD/pcS-1	28.6	1.37
MP2/def2-SVP	27.9	1.38
MP2/def2-TZVP	32.8	1.71
MP2/pcS-1	31.4	1.48
MP2/pcS-2	34.3	1.67
B97-2/def2-SVP	29.1	1.34
B97-2/pcS-1	31.0	1.43
B97-2/pcS-2	33.8	1.69
B97-2/pcS-3	33.7	1.59

laboratories. To determine the influence of the solvent on the outcome of the chemical shift calculations, two solvation

schemes were used: (1) the C-PCM^{38,39} solvation model for only NMR calculation and (2) for both NMR (C-PCM) and preceding geometry optimization (COSMO³⁹). The results of these calculations show that the influence of the solvent on the ^1H NMR and ^{13}C NMR spectra seems negligible. The use of explicit solvent molecules is not expected to be necessary because the twistane systems do not show substantial solvent–solute interaction, such as hydrogen bonding. Therefore, all further computations were performed without consideration of solvation. In the next step, different levels of theory (HF/def2-TZVP, B3LYP/def2-TZVP, KT2/def2-TZVP, B97-2/def2-TZVP, B97-2/pcS-1, B97-2/pcS-2, MP2/def2-TZVP, MP2/pcS-1, and CCSD/pcS-1) were investigated to determine an appropriate method for the NMR calculation of polytwistane (1). Figure 5 shows that compared to other tested DFT functionals and HF, the B97-2 approach produces values in slightly better agreement with the CCSD/pcS-1 values (MAD = 0.1 ppm for C atoms, and MAD = 0.02 for H atoms) as well as with the experimental values (for more details, see the Supporting Information).

The difference between the B97-2 and MP2 results is small (~ 0.4 ppm for ^{13}C NMR), although the MP2 calculations are much more expensive. Therefore, we decided to use the B97-2 approach for the large oligotwistanes. Considering the economical use of computational power, the pcS-1 basis set introduced by Jensen²⁹ was chosen, as it shows accuracy similar to that of def2-TZVP but is considerably less expensive.¹⁸ Therefore, the B97-2/pcS-1 approach can be efficiently used for further NMR calculations of the large oligotwistanes. This statement is also in accordance with a recent study by Flaig et

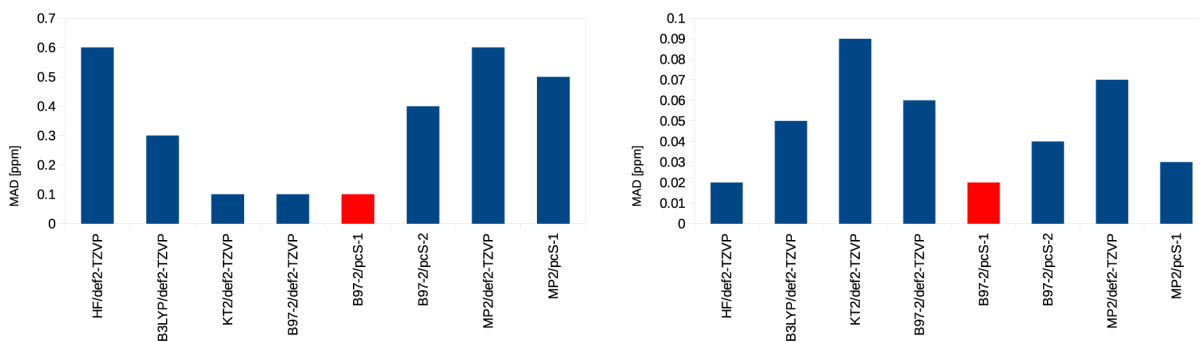


Figure 5. Mean absolute deviations (MAD) for the ^{13}C (left) and ^1H (right) NMR shifts of twistane at different levels of theory with respect to CCSD/pcS-1 results. All calculations were performed using the intermediate reference method [with twistane as the intermediate reference calculated at the CCSD(T)/pcS-1 level of theory].

al.¹⁸ In addition, the appropriate method for geometry optimization was determined. Three DFT methods (B3LYP/def2-TZVP, PBE0/def2-TZVP, and PBE0-D3/def2-TZVP) were compared to the RI-MP2/def2-TZVP approach. The results are listed in Table 3. Among the tested DFT-optimized

Table 3. MADs from the Experiment of the ^{13}C and ^1H NMR Chemical Shifts of Tritwistane Calculated at the B97-2/pcS-1 Level of Theory Using Different Levels of Theory for the Geometry Optimization of Tritwistane and Root-Mean-Square Deviations (RMSD) between RI-MP2/def2-TZVP and DFT-Optimized Structures

	RI-MP2	B3LYP	PBE0	PBE0-D3
RMSD (Å)		0.02854	0.01107	0.00852
^{13}C MAD (ppm)	0.8	0.8	0.8	0.7
^1H MAD (ppm)	0.21	0.23	0.22	0.23

structures, the PBE0-D3/def2-TZVP method shows the smallest root-mean-square deviation (RMSD) from the RI-MP2/def2-TZVP structure. However, the influence of the geometry optimization method on the NMR chemical shift calculation is rather small. The expensive RI-MP2/def2-TZVP level was chosen for the smaller oligotwistane $\text{C}_{46}\text{H}_{52}$ and the PBE0-D3/def2-TZVP level for oligotwistanes $\text{C}_{46}\text{H}_{52}$ and $\text{C}_{86}\text{H}_{92}$.

The calculations for oligotwistanes $\text{C}_{46}\text{H}_{52}$ (Figure 6) and $\text{C}_{86}\text{H}_{92}$ clearly show the convergence of the NMR chemical shift of the methines with increasing distance to the termini. The difference between the converged chemical shifts for these two systems is negligible: 0.01 ppm for the ^{13}C and 0.001 ppm for the ^1H chemical shifts (see the Supporting Information). Because we can assume that no significant change in the chemical environment should occur in proceeding from $\text{C}_{46}\text{H}_{52}$ and $\text{C}_{86}\text{H}_{92}$ to polytwistane (1), the NMR spectra of polytwistane (1) can be expected to exhibit one signal at 1.46 ppm (^1H NMR) and one signal at 34.5 ppm (^{13}C NMR).

A comparison of the two computational approaches shows that both offer attractive features. The first strategy employs the calculation versus experiment calibration with systems of the same nature. The latter can effectively cancel methodical errors. However, the quantum chemical levels suggested by Lodewyk et al.¹⁶ [B3LYP/6-31+G(d,p)-CPCM//B3LYP/6-31G(d)] can be insufficient for some systems, requiring for instance a better description of the structure or more sophisticated basis sets.

The second approach is not biased by experiment and exploits a level of theory that was thoroughly selected after comparison of various computational methods, including CCSD calculations. The combination of the B97-2 DFT functional with the pcS-1 basis set, which was suggested especially for the NMR chemical shift calculations, reaches the lowest deviation as compared to both experiment and high-level theory (CCSD). The independence from experimental data increases the general applicability of this approach. Furthermore, this independence can be a reason for the distinct difference of 0.43 ppm (23% deviation) in the ^1H NMR chemical shift compared to the values obtained by the linear regression method within the B3LYP/6-31+G(d,p)-CPCM//B3LYP/6-31G(d) level of theory.

As a consequence, a third alternative is to combine the higher level of theory with the empirical corrections. With this approach, the NMR properties were calculated for the same set of compounds used for the first linear regression at the B97-2/pcS-1//RI-MP2/def2-TZVP and B97-2/pcS-1//PBE0-D3/def2-TZVP levels of theory.

Table 4 lists the results obtained from all tested approaches: Methods 1 and 3 are the linear regression approaches using different quantum chemical levels. Methods 2a and 2b exploit twistane as the intermediate reference with its NMR chemical shifts either calculated at the CCSD(T)/pcS-1 level of theory (nonempirical method 2a) or experimentally measured³⁷ (method 2b). In ^{13}C NMR, all the methods show close accordance with an absolute difference of 2.2 ppm (7%). Overall, our most reliable computed data predict the NMR chemical shifts of polytwistane (1) to be ~ 1.5 ppm for ^1H and ~ 33 ppm for ^{13}C . These predicted data are expected to simplify the identification of polytwistane (1).

4. CALCULATION OF THE NMR CHEMICAL SHIFTS OF RELATED sp^3 HYDROCARBON NANORODS

Recently, Fitzgibbons et al.⁴ reported experimental results for a crystalline one-dimensional sp^3 carbon nanomaterial formed by high-pressure solid-state polymerization of benzene. ^{13}C solid-state NMR of this material shows a strong peak around 40 ppm. Fitzgibbons et al.⁴ assign this peak to a proposed structure of an sp^3 -hybridized hydrocarbon nanorod, although definitive evidence of this in the form of, e.g., an X-ray crystal structure is not presented. Moreover, the appearance of the reported signals indicates that the product is not monostructural but may

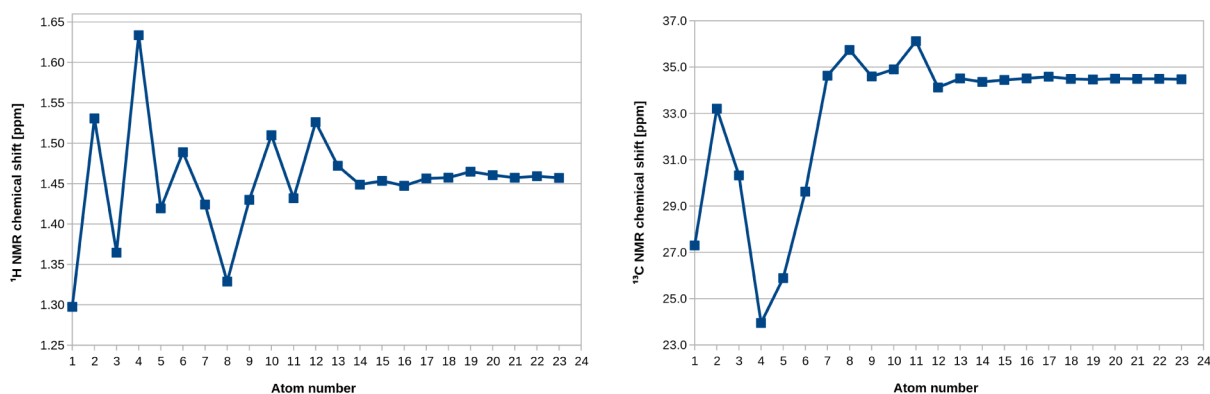
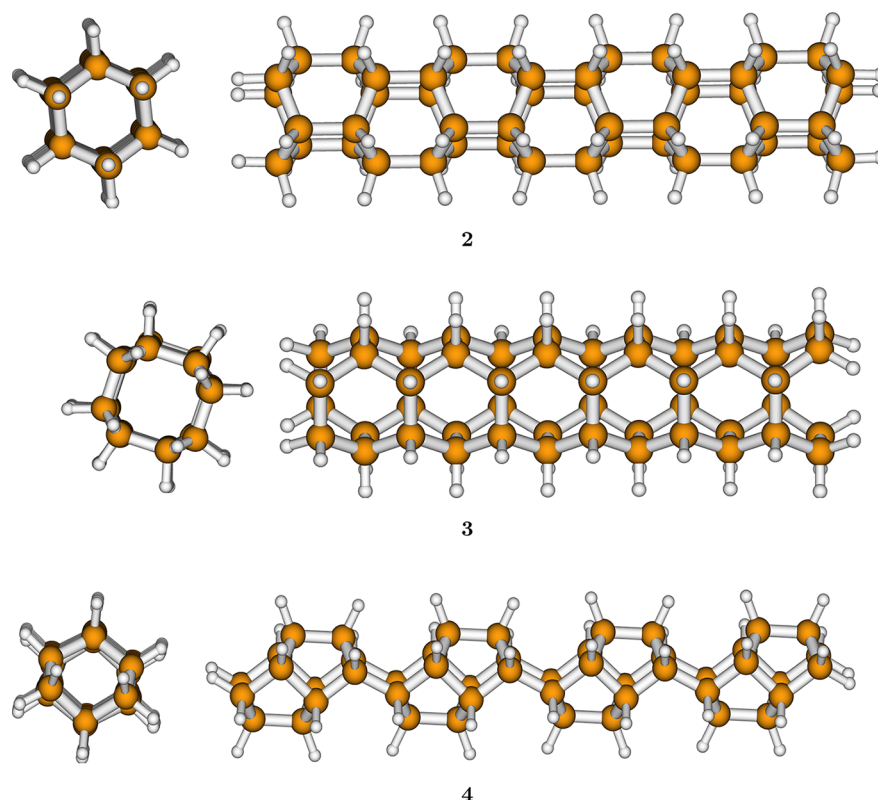


Figure 6. Calculated ^1H and ^{13}C NMR chemical shifts corresponding to the atom number specified in $\text{C}_{46}\text{H}_{52}$ oligotwistane (Figure 2). The shifts were obtained at the B97-2/pcS-1/RI-MP2/def2-TZVP level of theory by applying the intermediate reference method [with twistane as the intermediate reference calculated at the CCSD(T)/pcS-1 level of theory].

Table 4. Calculated ^1H and ^{13}C NMR Chemical Shifts Expected for the Infinite Polytwistane (1)^a

NMR	method 1 (linear regression)	method 2a [nonempirical, intermediate reference: twistane, CCSD(T)/pcS-1]		method 2b (intermediate reference: twistane, experiment)		method 3 (linear regression)	
	B3LYP/6-31+G(d,p)-CPCM	B97-2/pcS-1		B97-2/pcS-1		B97-2/pcS-1	
	B3LYP/6-31G(d)	RI-MP2/def2-TZVP	PBE0-D3/def2-TZVP	RI-MP2/def2-TZVP	PBE0-D3/def2-TZVP	RI-MP2/def2-TZVP	PBE0-D3/def2-TZVP
geometry	B3LYP/6-31G(d)						
^{13}C (ppm)	35.5	34.5	33.7	33.5	33.0	33.3	33.1
^1H (ppm)	1.9	1.5	1.4	1.4–1.7	1.4–1.7	1.5	1.5

^aDifferent computational approaches in comparison.**Figure 7.** Fragments of three sp^3 carbon nanostructures suggested by Fitzgibbons et al.⁴ and Stojkovic et al.⁴⁰ All structures were optimized at the PBE0-D3/def2-TZVP level of theory in this work.

consist of different sp^3 hydrocarbon nanorods. Having established a reliable computational scheme for the NMR calculation of a similar structure, we apply this method in the following to other related proposed structures of hydrocarbon nanorods. This may shed some light on the composition of the product from the recently reported high-pressure benzene polymerization. We apply our computational approach to three nanostructures suggested by Fitzgibbons et al.⁴ and Stojkovic et al.⁴⁰ Figure 7 shows the structures of oligomers corresponding to these three nanotubes, while Table 5 lists the ^{13}C and ^1H

Table 5. ^{13}C and ^1H NMR Chemical Shifts of Four Different sp^3 Carbon Nanostructures As Obtained at the B97-2/pcS-1//PBE0-D3/def2-TZVP Level of Theory by Applying the Linear Regression Approach

	1	2	3	4	experiment
^{13}C (ppm)	33.1	28.6	35.5	56.0, 44.5, 40.4, 44.2	~40
^1H (ppm)	1.5	2.1	1.6	2.0, 2.5, 2.4, 2.4	

chemical shifts for all four [including polytwistane (1)] sp^3 systems. In Figure 8, the experimental NMR spectrum disclosed by Fitzgibbons et al.⁴ is compared with the calculated signals of structures 1–4. The results indicate that systems 2 and 4 seem the least probable structural fragments of the nanorods: the 28.6 ppm signal of nanotube 2 is more than 10 ppm from the experimental peak; among the four signals of structure 4, there is a signal at 56.0 ppm, which is not found in the experimental NMR spectrum. On the other hand, polytwistane (1) and nanotube 3 may be potential candidates to be part of the reported product mixture. Nevertheless, it has to be stressed that a reliable identification of the carbon nanothreads by Fitzgibbons et al.⁴ remains a challenge, because the error bars should be kept in mind. Therefore, more experimental data would be needed for a reliable identification in the future.

5. CONCLUSION

In this work, we compare different computational approaches for calculating ^{13}C and ^1H NMR chemical shifts of infinite

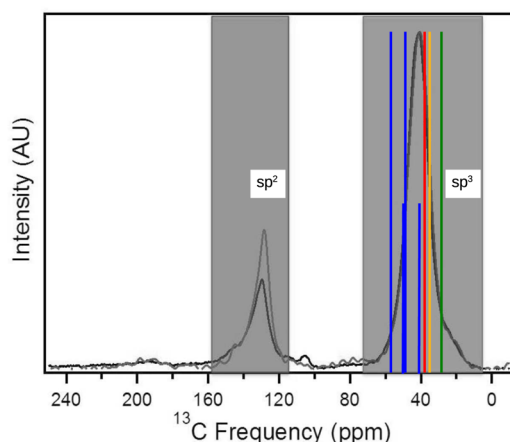


Figure 8. Experimental NMR spectrum measured by Fitzgibbons et al.⁴ compared with the calculated ^{13}C NMR signals for four sp^3 carbon nanostructures: 1 (polytwistane, yellow), 2 (green), 3 (red), and 4 (blue). The experimental spectrum is adapted by permission from Macmillan Publishers Ltd⁴ and shows traces of a ^{13}CD (gray) and a ^{13}CH (black) sample of high-pressure benzene polymerization products. The nanowires have both sp^3 (dominant, 80–84%) and sp^2 contents, which is apparent from the experimental spectrum.⁴

polytwistane (1). Comparison of different DFT functionals with wave function-based methods reveals that GIAO-B97-2/pcS-1//PBE0-D3/def2-TZVP seems to be the best compromise between accuracy and computational cost. Accurate prediction of NMR chemical shifts of polytwistane (1) and related systems requires an intermediate reference system (if approximative quantum chemical methods, such as DFT, need to be employed for large molecules) or application of linear regression schemes. Both approaches provide similar ^{13}C and ^1H NMR chemical shifts at the B97-2/pcS-1 level of theory. The convergence of the chemical shifts with the size of the system is observed starting from the $\text{C}_{46}\text{H}_{52}$ oligotwistane. The calculated chemical shift values do not change passing from the $\text{C}_{46}\text{H}_{52}$ oligotwistane to the larger $\text{C}_{86}\text{H}_{92}$ oligotwistane. The converged values of 1.5 and 33 ppm for ^1H and ^{13}C NMR chemical shifts, respectively, are expected to represent the NMR spectrum of infinite polytwistane. Finally, the elaborated computational procedure was applied for different sp^3 carbon nanostructures. These results are compared to recently reported experimental data of new sp^3 nanomaterials resulting from the high-pressure polymerization of benzene. Our analysis shows that polytwistane (1) might be a possible structural fragment of the synthesized nanorods.

■ ASSOCIATED CONTENT

Supporting Information

Experimental and calculated NMR chemical shifts as well as Cartesian coordinates for all the systems in this work and experimental procedures, NMR spectra, and crystallographic data for the previously unpublished systems. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: dirk.trauner@cup.uni-muenchen.de.

*E-mail: christian.ochsenfeld@uni-muenchen.de.

Author Contributions

B.M. and M.O. contributed equally to this work.

Funding

We acknowledge financial support by the SFB 749 “Dynamik und Intermediate molekularer Transformationen” (DFG) and the DFG cluster of excellence EXC 114 “Center for Integrated Protein Science Munich” (CIPSM).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Dr. Peter Mayer is gratefully acknowledged for X-ray crystallography. We also thank Pascal Ellerbrock and Dr. David M. Barber for helpful discussions during the preparation of the manuscript.

■ REFERENCES

- (1) Barua, S. R.; Quanz, H.; Olbrich, M.; Schreiner, P. R.; Trauner, D.; Allen, W. D. *Chem.—Eur. J.* **2014**, *20*, 1638–1645.
- (2) Wheeler, S. E.; Houk, K. N.; Schleyer, P. v. R.; Allen, W. D. *J. Am. Chem. Soc.* **2009**, *131*, 2547–2560.
- (3) Olbrich, M.; Mayer, P.; Trauner, D. *Org. Biomol. Chem.* **2014**, *12*, 108–112.
- (4) Fitzgibbons, T. C.; Guthrie, M.; Xu, E.-s.; Crespi, V. H.; Davidowski, S. K.; Cody, G. D.; Alem, N.; Badding, J. V. *Nat. Mater.* **2015**, *14*, 43–47.
- (5) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789–807.
- (6) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251–8260.
- (7) Häser, M.; Ahlrichs, R.; Baron, H. P.; Weis, P.; Horn, H. *Theor. Chim. Acta* **1992**, *83*, 455–470.
- (8) Wolff, S. K.; Ziegler, T. *J. Chem. Phys.* **1998**, *109*, 895–905.
- (9) Gauss, J. *J. Chem. Phys.* **1993**, *99*, 3629–3643.
- (10) Kollwitz, M.; Gauss, J. *Chem. Phys. Lett.* **1996**, *260*, 639–646.
- (11) Kollwitz, M.; Häser, M.; Gauss, J. *J. Chem. Phys.* **1998**, *108*, 8295–8301.
- (12) Gauss, J.; Stanton, J. F. *J. Chem. Phys.* **1995**, *103*, 3561–3577.
- (13) Gauss, J.; Stanton, J. F. *Chem. Phys. Lett.* **1997**, *276*, 70–77.
- (14) Ochsenfeld, C.; Kussmann, J.; Koziol, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 4485–4489.
- (15) Kussmann, J.; Ochsenfeld, C. *J. Chem. Phys.* **2007**, *127*, 054103.
- (16) Lodewyk, M. W.; Siebert, M. R.; Tantillo, D. J. *Chem. Rev.* **2012**, *112*, 1839–1862.
- (17) Teale, A. M.; Lutnes, O. B.; Helgaker, T.; Tozer, D. J.; Gauss, J. *J. Chem. Phys.* **2013**, *138*, 024111.
- (18) Flaig, D.; Maurer, M.; Hanni, M.; Braunger, K.; Kick, L.; Thubauville, M.; Ochsenfeld, C. *J. Chem. Theory Comput.* **2014**, *10*, 572–578.
- (19) London, F. *J. Phys. Radium* **1937**, *8*, 397–409.
- (20) Weigend, F.; Häser, M. *Theor. Chim. Acta* **1997**, *97*, 331–340.
- (21) Weigend, F.; Häser, M.; Patzelt, H.; Ahlrichs, R. *Chem. Phys. Lett.* **1998**, *294*, 143–152.
- (22) Adamo, C.; Scuseria, G. E.; Barone, V. *J. Chem. Phys.* **1999**, *111*, 2889–2899.
- (23) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.
- (24) Wilson, P. J.; Bradley, T. J.; Tozer, D. J. *J. Chem. Phys.* **2001**, *115*, 9233–9242.
- (25) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623–11627.
- (26) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372–1377.
- (27) Keal, T. W.; Tozer, D. J. *J. Chem. Phys.* **2003**, *119*, 3015–3024.
- (28) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- (29) Jensen, F. *J. Chem. Theory Comput.* **2008**, *4*, 719–727.
- (30) TURBOMOLE, version 6.3 2011, a development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007, available from <http://www.turbomole.com>.

- (31) CFOUR, a quantum chemical program package written by J. F. Stanton, J. Gauss, M. E. Harding, and P. G. Szalay, with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, D. A. Matthews, T. Metzroth, D. P. O'Neill, D. R. Price, E. Prochnow, K. Ruud, F. Schiffmann, S. Stopkowitz, A. Tajti, J. Vázquez, F. Wang, and J. D. Watts. Integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), and ABACUS (T. Helgaker, H. J. A. Jensen, P. Jørgensen, and J. Olsen) and ECP routines by A. V. Mitin and C. van Wüllen. For the current version, see <http://www.cfour.de>.
- (32) Development version of Q-Chem (www.q-chem.com).
- (33) Kussmann, J.; Ochsenfeld, C. *J. Chem. Phys.* **2013**, *138*, 134114.
- (34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.
- (35) Ochsenfeld, C.; Koziol, F.; Brown, S. P.; Schaller, T.; Seelbach, U. P.; Klärner, F.-G. *Solid State Nucl. Magn. Reson.* **2002**, *22*, 128–153.
- (36) Zienau, J.; Kussmann, J.; Ochsenfeld, C. *Mol. Phys.* **2010**, *108*, 333–342.
- (37) Beierbeck, H.; Saunders, J. K. *Can. J. Chem.* **1977**, *55*, 3161–3165.
- (38) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995–2001.
- (39) Klamt, A.; Schüürmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799–805.
- (40) Stojkovic, D.; Zhang, P.; Crespi, V. *Phys. Rev. Lett.* **2001**, *87*, 125502.