Theor Chem Account (2008) 121:53–57
DOI 10.1007/s00214-008-0447-2

REGULAR ARTICLE

Effect of molecular size on the parity-non-conserving contributions to the nuclear magnetic resonance shielding constant

Ville Weijo · Pekka Manninen · Juha Vaara

Received: 19 March 2008 / Accepted: 7 April 2008 / Published online: 22 April 2008

Abstract We present density-functional theory studies on the effects of molecular size on the parity-violating contribution to the nuclear magnetic shielding constant. We focus on models with different backbone and side chain lengths, as well as the details of geometry optimization for certain helical polysilylenes and investigate the parity-violating contribution to the shielding constant of the ^{29}Si nucleus of the backbone. Our calculations show that the molecular geometry has a large influence on the magnitude of the parity-violating shielding contribution, a result that is in line with the previous studies on much smaller molecules. In addition, we find convergence in the magnitude of the PV effect with respect to system size, when using geometries that preserve the helical Si backbone structure optimized for the largest of the present systems. This can be interpreted in terms of the non-size-extensive nature of the parity-violating operator influencing the leading-order effect on nuclear magnetic shielding, as opposed to the size-extensive interaction affecting the energy difference between enantiomers. Our molecules are truncated models of large polysilylene systems, for which a difference in the ^{29}Si chemical shift between enantiomers has been observed to be 0.06 ppm (Fujiki in Macromol Rapid Commun 22, 669–674, 2001). As expected based on earlier first principles studies of small molecules, we do not find support for the difference to be of the parity-violating origin. Instead, the predicted parity-violation-induced splitting of the ^{29}Si resonance is found to converge at values around 10^{-8} ppm with increasingly large Si backbone.

Keywords Molecular parity violation

1 Introduction

Molecular magnetic properties have been considered from a theoretical point of view as a conceivable tool for observing parity-violating (PV) effects in molecules [1–10]. Previous first principles studies have concentrated on small molecules such as hydrogen dichalcogens and different technical aspects of electronic structure calculation. It has been found from the studies of these model systems that the PV contribution to the nuclear magnetic resonance (NMR) shielding constant is very sensitive to variations of the dihedral angle [4,5,8–10]. However, systematic studies of how the PV contribution to the NMR shielding constant correlates with the large-scale molecular structure have not been carried out so far. PV contributions to the energy differences between the enantiomers of a chiral molecule are size-extensive (for a review of the PV energy differences, see e.g., Ref. [11]). This is due to the fact that they involve a sum of the PV interaction between electrons and the different nuclei of the molecule. In contrast, long-distance direct electronic structure effects are unlikely to affect the PV contribution to NMR properties since the leading-order effects on them only feature the interaction at the nucleus in question (see, e.g., Ref. [6]).

Electronic supplementary material The online version of this article (doi:10.1007/s00214-008-0447-2) contains supplementary material, which is available to authorized users.

V. Weijo
Laboratory of Physics, Helsinki University of Technology,
P. O. Box 1100, Otakaari 1 M, 02015 Espoo, Finland

P. Manninen
Center for High-Performance Computing and Networking CSC,
P. O. Box 405, 02101 Espoo, Finland

J. Vaara · V. Weijo (✉)
Laboratory of Physical Chemistry, Department of Chemistry,
University of Helsinki, P. O. Box 55,
A.I. Virtasen aukio 1, 00014 Helsinki, Finland
e-mail: ville.weijo@helsinki.fi

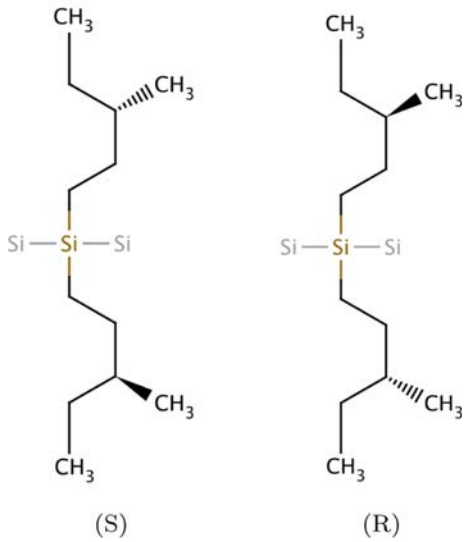

Fig. 1 *S*- and *R*-enantiomeric structures of the polysilylene in question (see text for details)

Consequently, the PV effects on NMR properties are not size-extensive.

In this paper we address the effect of molecular structure on the PV contributions to ^{29}Si shielding constant using density-functional theory (DFT). The studied molecules are enantiomeric pairs of poly[bis{(*S*)-3,7-dimethyloctyl} silylene] and poly[bis{(*R*)-3,7-dimethyloctyl}silylene] with varying models for the side chains and Si backbone. The *R*- and *S*-enantiomeric side chains associated with one Si atom are shown in Fig. 1.

From the experimental point of view, a difference of 0.06 ppm between the chemical shift of the two enantiomers has been recorded in their ^{29}Si NMR spectra [12]. The observation is interesting, because that would be the way the ^{29}Si resonance would split under the influence of PV Z_0-boson exchange. In the light of theoretical estimates that range from 10^{-10} to 10^{-8} ppm for comparable, light nuclei [1–10], a PV origin of the splitting is *a priori* very unlikely, however. Indeed, we predict a PV splitting that is several orders of magnitude lower than the observed chemical shift difference. The details of the molecular model construction are found to be crucial for the calculated PV shielding effect, and the anticipated lack of extensivity with the system size is verified.

2 First-principles calculations

The non-relativistic leading-order PV contribution to the isotropic part of the NMR shielding tensor of nucleus K can be expressed as a linear response function (see, e.g., Ref. [6])

$$\sigma^{\mathrm{PV}}_{K,\epsilon\tau} = \frac{1}{\gamma_K}\left\langle\!\left\langle h^{\mathrm{PV}}_{K,\epsilon}; h^{\mathrm{OZ}}_{B_0,\tau}\right\rangle\!\right\rangle_0, \tag{1}$$

where the parity-violating operator is

$$h^{\mathrm{PV}}_{K,\epsilon} = -\frac{G_{\mathrm{F}}\alpha}{2\sqrt{2}}\lambda_K(1-4\sin^2\theta_{\mathrm{W}})\sum_i\left[-\mathrm{i}\nabla_{i,\epsilon},\delta(\mathbf{r}_{iK})\right]_+, \tag{2}$$

and the orbital Zeeman operator

$$h^{\mathrm{OZ}}_{B_0,\tau} = \frac{1}{2}\sum_i \ell_{iO,\tau}. \tag{3}$$

Equation (1) is the only leading-order contribution to the isotropic part of the tensor, if the gauge origin O is placed at the nucleus K. $\boldsymbol{\ell}_{iO}$ is the angular momentum operator of electron i with respect to O, and $\mathbf{r}_{iK}$ is the distance vector between electron i and nucleus K. γ_K and α are the gyromagnetic ratio of K and the fine structure constant, respectively. The weak coupling constant $G_{\mathrm{F}} = 2.22 \times 10^{-14}$ a.u. and the Weinberg angle is $\theta_{\mathrm{W}} = 0.2320$. λ_K is a nucleus-dependent factor that includes contributions from the nuclear structure and the nuclear anapole moment [13]. The λ_K are not usually known and are set to unity during the calculations. The SI-based atomic unit system is throughout this work.

It should be noted that the part of the PV operator relevant for the leading-order effect on shielding, Eq. (2), does not contain a sum over nuclei, in contrast to the operator used in PV energy calculations [14],

$$\sum_K Q_K \sum_i \mathbf{s}_i \cdot [-\mathrm{i}\nabla_i, \delta(\mathbf{r}_{iK})]_+,$$

where Q_K is the weak charge of K and $\mathbf{s}_i$ the spin of i. This imples that the PV NMR effect on an individual nucleus in Eq. (1) may be expected to saturate with increasing size of the molecule.

We evaluated using DFT the leading-order PV contributions [Eq. (1)] for the central ^{29}Si nucleus in helical polysilylene models containing one, three and five Si-atoms, denoted as Si-1, Si-3 and Si-5, respectively. Truncated *R*-type side chains of different lengths were attached to the backbone models. The basis sets used have Huzinaga exponents [15], are polarized and contracted by Kutzelnigg et al. [16], and are denoted as IGLO-II–IV, in the order of an increasing number of basis functions. Geometries were optimized with the Becke three-parameter hybrid functional (B3LYP) [17, 18] and SVP basis set [19] with the TURBOMOLE program package [20–22]. Property calculations were performed

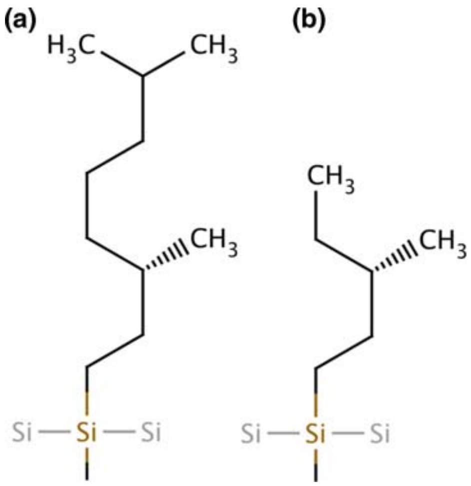

Fig. 2 Side chains of poly[bis{(*S*)-3,7-dimethyloctyl}silylene]: **a** Full, **b** truncated

using a local version of the DALTON quantum chemistry program [23]. The largest calculations on the Si-5 model had 197 atoms and 2,287 contracted basis functions. All the structures are deposited in the supporting information.[1]

3 Results and discussion

3.1 Effects of basis set and side chain truncation

We begin our investigation from a single-Si-atom unit of larger polysilylene chain, with the side chains in the *R*-configuration shown in Fig. 1. We have seen in previous studies [10] that B3LYP has at least qualitative predicting power as compared to more expensive and accurate methods, when it comes to PV contributions to the NMR shielding constant. Consequently, we use this functional for all the present calculations.

To study the possibility of reducing computational cost, we compare the results for a full-length side chain with the truncated one, illustrated in Fig. 2. The obtained basis sets dependence of the PV contribution is shown in Fig. 3 and the corresponding numerical data are listed in Table 1.

Clearly, the IGLO basis sets work rather well with the truncated side chains as there are only small changes between the IGLO-II and IGLO-IV results. In the full chains the basis set effect is larger and the PV contribution increases towards better basis sets. The increase is approximately 50% from IGLO-II to IGLO-IV, but the difference between IGLO-III and IGLO-IV is much less dramatic, about 10%.

The effect of truncation is large (see Fig. 3), decreasing the PV contribution approximately by a factor of two, when using a small basis set. Instead, if the truncated side chain is constructed without optimization after the truncation, by substituting the missing carbon–carbon bond by a carbon–hydrogen bond (length 1.1 Å), the difference in the PV contribution between the full and truncated chains is reduced to less than 1%. This implies that the difference is due to the strong dependence of the PV contribution on the molecular geometry rather than direct electronic structure effects.

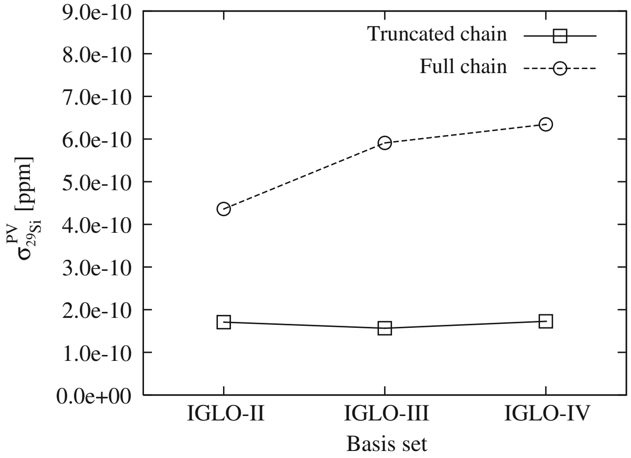

Fig. 3 Basis set dependence at the B3LYP level of the parity violation-induced enantiomeric splitting of the isotropic ^{29}Si shielding constant in the case of a single Si atom with full and truncated side chains

Table 1 Basis-set dependence of the PV contribution to the ^{29}Si shielding constant in the Si-1 model with full and truncated side chains

Side chain type	IGLO-II	IGLO-III	IGLO-IV
Truncated	1.71	1.57	1.73
Full	4.36	5.91	6.34

(All values in 10^{-10} ppm)

Due to the size of systems that we consider, we will use the truncated, reoptimized side chains with the IGLO-II basis and acknowledge that this choice can give rise to an error of a factor of two.

3.2 Effects of backbone structure

Two variants of the backbone structure are considered in the following. The first one, denoted as “Optimized”, refers to a full geometry-optimized version for each individual length of the backbone (Si-1, Si-3 and Si-5 models). In these structures, a truncated Si backbone is constructed by terminating with hydrogen atoms, truncated *R*-type side chains are attached, and a full geometry relaxation is subsequently performed. The problem with this approach is that one or three Si atoms constitutes an insufficient length for the backbone to approach the limiting behavior of the local helical geometry. Because of that, we consider also systems that are constructed using the Si-5 backbone[1]. In these “Si-5 backbone” structures, the Si chain is held fixed at the optimized

---

[1] Structures of molecules are included in Supporting information. Files with `frozen` in the filename are those with the Si-5 backbone.

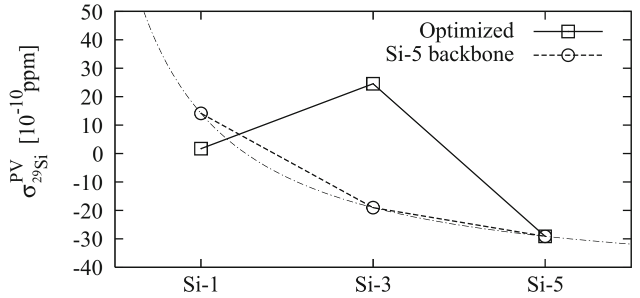

Fig. 4 Dependence of the parity-violating contribution (at the B3LYP/IGLO-II level) to the isotropic ^{29}Si shielding constant on the length and construction of the Si backbone. The side chains have the truncated and reoptimized *R*-enantiomeric structure. See text for details on "Optimized" and "Si-5 backbone". A smooth line has been fitted to the "Si-5 backbone" data to guide the eye

Table 2 Numerical values of PV-induced splittings to the isotropic ^{29}Si shielding constant for different lengths and structures of the Si-backbone (see text for details)

Structure	Si-1	Si-3	Si-5
Optimized	1.71	24.55	−29.10
Si-5 backbone	14.11	−19.01	−29.10

(All values in 10^{-10} ppm)

Si-5 geometry that adopts a P-type helix configuration where the two Si–Si–Si–Si dihedral angles are 163° and 165°. In the respective Si-3 and Si-1 structures, the outermost Si atoms are successively replaced by terminating hydrogens with the Si–H bonds (length 1.5 Å) oriented in the way that preserves the bond and dihedral angles of the backbone. The side chains are then attached and allowed to relax, while keeping the new backbone intact. In this way, we expect to see a more consistent progression in the PV contributions. The PV contribution is evaluated for the central ^{29}Si nucleus in each model.

Results with different chain lengths and types are shown in Fig. 4 and tabulated in Table 2. The fully optimized results show an irregular behavior. The most distinct feature is the sign difference between the Si-3 and Si-5 structures, which implies a strong dependence of the PV contribution on the molecular geometry near the central Si atom. The series of results with the Si-5 backbone, which simulates the dependence on the amount of neighboring atoms rather than on the local geometry, shows a more convincing trend. Although the contribution in Si-1 is of different sign than those in Si-3 and Si-5, the difference between Si-3 and Si-5 is considerably smaller, 10×10^{-10} ppm, than the difference between Si-1 and Si-3, 33×10^{-10} ppm.

The PV contribution is seen to saturate with the number of Si atoms in the backbone. Judging visually based on the three computational "Si-5 backbone" points, the infinite-chain limit would be about 50×10^{-10} ppm, corresponding to a 10^{-8} ppm splitting in the experimental peak positions between the *S*- and *R*-enantiomers. Consequently, saturation of the leading-order PV shielding effect is found as expected because Eq. (1) does not involve a sum over atomic nuclei, in contrast to the PV energy contributions [14].

3.3 Connection to experiment

As compared to the experimental observation of 0.06 ppm [12], our data are approximately seven orders of magnitude smaller. Besides errors from basis set (at most a factor of two) and the differences arising from the construction of the side chains (factor of three), there are relativistic effects to be considered [9,10]. A "prototypic" molecule comparable to our Si chains containing first and second-row atoms, is H_2S_2. In that system, the spin-orbit interaction reduces $\sigma^{PV}_{^{33}S}$ by a factor of two. If one would consider the relativistic factor of two to be increasing the contribution, take into account basis set and side chain errors, use the extrapolated chain length limit and expect an order of magnitude increase from the nucleus-dependent factor λ_K, we would gain about two orders of magnitude as compared to our initial estimate. Even in this scheme, a difference of five orders of magnitude remains, which is clearly too much to reach a conceptual agreement between Fujiki's result and the PV origin of the effect.

4 Conclusions

We have examined the effect of molecular model size and details of model construction on the non-size-extensive PV contribution to the NMR shielding constant of a ^{29}Si nucleus in helical polysilylenes. We find out that differences in local geometry can have a large impact on the magnitudes and signs of the PV contribution in realistic systems. We also find that the magnitude of the contribution increases with the Si backbone length, but saturates quickly by about five Si atoms. Using the results, we could estimate the PV-induced spectral splitting of ^{29}Si in systems where Fujiki [12] observed a difference of 0.06 ppm between the two enantiomers. Our best estimates of the PV effect are five orders of magnitude smaller than Fujiki's observation. Consequently, and in agreement with earlier first principles studies of other systems, it is very unlikely that the observation in Ref. [12] is of PV origin.

Acknowledgments H. Konschin, M. Straka and J. Sipilä (University of Helsinki) are thanked for useful discussions. One of the authors (VW) acknowledges financial support from the Jenny and Antti Wihuri Fund. JV is with the Finnish Center of Excellence in Computational Molecular Science (CMS) and acknowledges further support from the Emil Aaltonen Foundation. Computational resources were partially provided by CSC, the Finnish IT center for science (Espoo, Finland).

References

1. Barra AL, Robert JB, Wiesenfeld L (1986) Phys Lett A 115:443
2. Barra AL, Robert JB, Wiesenfeld L (1988) Europhys Lett 5:217
3. Barra AL, Robert JB (1996) Mol Phys 88:875
4. Soncini A, Faglioni F, Lazzeretti P (2003) Phys Rev A 68:033402
5. Laubender G, Berger R (2003) Chem Phys Chem 4:395
6. Weijo V, Manninen P, Vaara J (2005) J Chem Phys 123:054501
7. Weijo V, Manninen P (2006) Chem Phys Lett 433:37
8. Laubender G, Berger R (2006) Phys Rev A 74:032105
9. Bast R, Schwerdtfeger P, Saue T (2006) J Chem Phys 125:064504
10. Weijo V, Bast R, Manninen P, Saue T, Vaara J (2007) J Chem Phys 126:074107
11. Crassous J, Chardonnet C, Saue T, Schwerdtfeger P (2005) Org Biomol Chem 3:2218
12. Fujiki M (2001) Macromol Rapid Commun 22:669
13. Zel'dovich YB (1960) Zh Eksp Teor Fiz 39:1115
14. Hegstrom RA, Rein DW, Sandars PGH (1980) J Chem Phys 73:2329
15. Huzinaga S (1971) Approximate atomic functions. University of Alberta, Edmonton
16. Kutzelnigg W, Fleischer U, Schindler M (1990) The IGLO-Method: Ab-initio Calculation and Interpretation of NMR chemical shifts and magnetic susceptibilities. In: Diehl P, Flück E, Günther H, Kosfeld R, Seelig J (eds) NMR basic principles and progress, vol 23. Springer, Berlin
17. Becke AD (1993) J Chem Phys 98:5648
18. Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ (1994) J Phys Chem 98:11623
19. Schäfer A, Horn H, Ahlrichs R (1992) J Chem Phys 97:2571
20. Ahlrichs R, Bär M, Häser M, Horn M, Kölmel C (1989) Electronic structure calculations on workstation computers: The Program System TURBOMOLE V5.9. Chem Phys Lett 162:165
21. Treutler O, Ahlrichs R (1995) J Chem Phys 102:346
22. Deglmann P, Furche F, Ahlrichs R (2002) Chem Phys Lett 362:511
23. DALTON, a molecular electronic structure program, Release 2.0 (2005) see http://www.kjemi.uio.no/software/dalton/dalton.html