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Optimized ladder C and ladder H models for sigma conjugation: chain segmentation in polysilanes[†]

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ABSTRACT: The parameters of the Hückel type ladder C and ladder H models of permethylated oligosilanes have been optimized to reproduce orbital energies obtained from *ab initio* Hartree–Fock (HF) calculations of 84 conformers with 1–8 silicon atoms at their optimized geometries. With the optimized parameters, the ladder models reproduce the top ~5% of the *ab initio* occupied orbital energies with a mean error of 0.03–0.05 eV. Using Koopmans' theorem, trends in the ionization potentials of very long oligosilanes and polysilanes, including their conformational dependence, can now be predicted with the accuracy of the HF/TZ *ab initio* method. We use the ladder models to examine the chain-length dependence of conformational effects in chains with up to 40 silicon atoms, with particular attention to the issue of conformationally induced chain segmentation. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: sigma conjugation; polysilanes; chain segmentation; sigma delocalization; orbital energies; ladder C model; ladder H model; Sandorfy model

INTRODUCTION

σ-Conjugated polysilanes possess a number of intriguing optical and charge-transport properties which have fueled their extensive experimental and theoretical examination.[1,2] Phenomena such as thermochromism,[3,4] piezochromism,[5] ionochromism[6] and solvatochromism[7] are believed to be caused by the conformational dependence of the electronic structure. According to the segmentation model of polysilanes,[8] the chain can be thought of as a collection of linked weakly interacting oligosilane segments defined by conformational twists in the polymer backbone and changing in time as the conformation changes. These segments are believed to serve as carriers of charge and excitation and can be modeled by short oligosilanes. It is therefore of interest to understand the UV absorption spectra and ionization potentials of oligosilanes in the hope of ultimately predicting the optical and charge-transport properties of the polymers as a function of conformation. An important part of this program is the prediction of orbital energies, which are related to ionization potentials through Koopmans' theorem. Although non-Koopmans' terms are far from negligible, they are roughly constant, and *ab initio* Hartree–Fock orbital energies show fairly good agreement with measured ionization potentials.[9–11] Subsequently, the prediction of electronic excitation energies may be attempted. Even for short chains, accurate calculation of absorption spectra is quite difficult.[12–14]

We see two reasons for which it is desirable to have a simple computational model for orbital energies and, ultimately, excitation energies. First, it might provide some intuitive understanding of the conformational and chain-length effects on the electronic structure of the polysilanes, and second, it might permit computations for very long chains encountered in the polysilane high polymers. This provided the motivation for the present work.

Previous work started from the Sandorfy C model, originally developed for hydrocarbons.[15] This model was extended and brought to the PPP level,[16–20] but none of these improved methods considered the effect of the conformational dependence of the one-electron part of the semiempirical Hamiltonian. We proposed the ladder C and ladder H models,[21,22] which include a conformationally dependent term. The ladder C model with simply optimized parameters seemed to account for some of the spectral observations for conformational effects available at the time.[22]

In the present paper, we optimize the parameters of the ladder C and ladder H models thoroughly by comparing their results with orbital energies obtained from Hartree–Fock (HF) *ab initio* calculations for a large number of oligosilane conformers.

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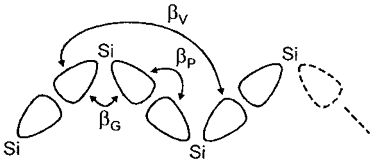

Figure 1. Basis set and resonance integrals in the ladder C model

METHODS

HF 3–21G* optimized geometries of a set of 87 conformers of Si_nMe_{2n+2}, $n = 1$, 2, 3, 4,[22] 5,[23] 6,[24] 7 (C.-H. Ottosson, H. Fogarty, R. Crespo and J. Michl, unpublished results), and 8 (C.-H. Ottosson, H. Fogarty, R. Crespo and J. Michl, unpublished results) were used to perform single-point HF calculations with the 6–31G* basis set to obtain orbital energies. These will be referred to as DZ (double zeta) orbital energies. Optimized geometries (C.-H. Ottosson, H. Fogarty, R. Crespo and J. Michl, unpublished results) of a second set of 29 conformers of Si_nMe_{2n+2}, $n = 1$–6, were obtained at the Møller–Plesset pertubation theory level (MP2) with the 6–311G* basis set for silicon atoms, the 6–31G* basis set for carbon atoms and the 6–31G basis set for hydrogen atoms, and were used to obtain HF orbital energies with this basis set. These will be referred to as triple zeta (TZ) orbital energies. A third set of data consists of experimental ionization potentials for 13 molecules,[9,10,22,25,26] only five of which are permethylated oligosilanes[25,26] (a constant value of 0.7 eV was added to the values reported in Ref. 25 to make them compatible with the photoelectron values in Ref. 26), the rest containing various saturated cyclic substituents that limit conformational freedom.[9,10]

To fit the Hückel orbital energies to the *ab initio* orbital energies, a program was written in Fortran77 to perform the Hückel calculations and the parameter optimizations using Powell's direction-set algorithm[27] on a Gateway 7400 server. The error function is the square root of the sum of the r.m.s. deviations of the calculated Hückel orbital energies from the *ab initio* orbital energies or experimental ionization energies.

The basis set for the ladder C model (Fig. 1) consists of two sp^3 hybrid orbitals in the backbone for each internal silicon atom and a single sp^3 orbital for the terminal silicon atoms. In the model Hamiltonian, four different types of integrals are considered. The Coulomb integral α_{Si} describes the electronegativity of the silicon sp^3 hybrid orbital. The resonance integral β_P describes the primary bonding interaction between two basis set orbitals facing each other in an Si—Si bond. The resonance integral β_G describes the geminal interaction between two sp^3 orbitals on the same silicon atom. The resonance integral β_V describes the vicinal interaction between two orbitals located on two neighboring silicon atoms and not facing each other. It is the only parameter of the model that depends on the dihedral angle.

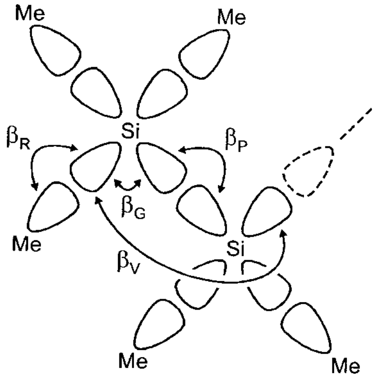

Figure 2. Basis set and resonance integrals in the ladder H model

In the ladder H model, all four valence-shell sp^3 hybrid orbitals of each silicon atom are included as well as one hybrid orbital of each carbon atom pointing towards a silicon atom (Fig. 2). The model Hamiltonian contains two types of Coulomb and four types of resonance integrals (Fig. 2). The Coulomb integrals over the sp^3 hybrid orbital located on silicon and carbon atoms are α_{Si} and α_C, respectively. The resonance integrals between two orbitals facing each other in an Si—Si and Si—C bond are β_P and β_R, respectively (primary interactions). The integral between two neighboring orbitals on one silicon atom is β_G (geminal interaction). The integral between two orbitals on neighboring silicon atoms that do not point at each other is β_V (vicinal interaction).

Previous studies[22] showed that the dependence of β_V on the dihedral angle ω is satisfactorily described by a cosine function, $\beta_V = C_1 + C_2\cos\omega$. Accordingly, C_1 and C_2 were used as the fitting parameters for β_V. In both models, only the backbone dihedral angles in a molecule have to be specified to define a conformation since the parameter β_V is the only geometry dependent quantity.

RESULTS

We determined the Hückel parameters for all six combinations of the three available orbital energy sets and the two different Hamiltonians and used the results to examine the properties of some permethylated oligosilanes with up to 40 silicon atoms, which is more than could be easily examined in an *ab initio* manner.

Matching of Hückel and *ab initio* orbitals

The correspondence of Hückel and *ab initio* orbitals was

Table 1. Optimized parameters for the ladder C, ladder H and Sandorfy C models of permethylated oligosilanes

		Parameter										Linear regression[a]					
Model		α_S	α_C	β_P	β_R	β_G	C_1[b]	C_2[b]	$\beta_V(0)$	$\beta_V(180)$	ω_0[c]	c	m	r	σ	N	ΔE
Ladder C	DZ	−6.6		−2.9		−1.1	0.12	−0.69	−0.57	0.81	80	0.3	1.03	0.9981	45	389	45
	TZ	−6.1		−3.5		−1.1	0.11	−0.70	−0.59	0.81	81	0.4	1.04	0.9982	44	100	47
	Exp	−5.1		−3.4		−0.8	0.02	−0.30	−0.28	0.32	86	−0.8	0.90	0.9489	171	32	142
Ladder H	DZ	−6.1	−9.4	−3.7	−4.0	−1.7	−0.18	−0.86	−1.04	0.68	102	−0.0	1.00	0.9987	35	389	27
	TZ	−6.5	−9.6	−3.2	−3.8	−1.8	−0.28	−0.99	−1.27	0.71	106	−0.1	0.99	0.9983	40	100	32
	Exp	−5.0	−6.5	−4.7	−5.2	−2.5	−0.45	−0.65	−1.10	0.20	134	−0.6	0.93	0.9616	212	48	176
Sandorfy C	DZ	−8.1		−1.4		−1.4						0.8	1.09	0.9742	179	386	179

[a] Parameters of the linear regression are c = offset (eV), m = slope, r = correlation coefficient, σ = standard deviation (meV), N = number of orbitals included in fitting/regression and ΔE = average error (meV).
[b] β_V is calculated from C_1 and C_2 according to $\beta_V = C_1 + C_2 \cos \omega$.
[c] ω_0 is the dihedral angle for which $\beta_V = 0$.

established by calculating the overlap S of all Hückel with all *ab initio* orbitals, where the latter were expressed in the valence part of Weinhold's natural hybrid orbital (NHO) basis.[28] For this purpose, the Hückel parameters optimized earlier[22] were taken as starting values. It was found that all orbitals with energies above -11 eV are in the same energy order in both methods, with typical S values of at least 0.6–0.9 and frequently above 0.9. These are about half of the occupied ladder C model orbitals, or a quarter of the ladder H model orbitals. Below -11 eV we find π-type orbitals, locally antisymmetric with respect to the Si—Si—Si plane. These fit worse, but are not important for optical or charge-transport properties. The poorer fit is understandable since the ladder model in its C approximation is incapable of describing π-type orbitals; in its H approximation it is capable of describing them, but the description is of limited quality since the hydrogen atoms, where a significant part of the *ab initio* wavefunction is located, are not considered explicitly.

Parameter fitting to *ab initio* calculations

Once the *ab initio* and Hückel orbitals are matched, it becomes possible to minimize the differences in their energies by a suitable choice of the Hückel parameters. This is done by looking for a minimum in the error function (root of the sum of mean square deviations in energy). The error function in the Hückel parameters space is very irregular and contains many different local minima of similar depth. Many of these are unphysical and were dismissed, although some produced a better fit than the minima with more reasonable parameter values. Many minima were always found which have only slightly differing parameter values. These are considered as one ill-defined shallow minimum. To obtain final parameter values, the values of 30 local minima considered to represent one shallow minimum were averaged and then used as a starting point in another reoptimization. The ladder C minima are generally much better defined than the ladder H minima as could be expected given a larger number of adjustable parameters in the latter. The fitting of the ladder H model to the TZ data was especially poorly defined, presumably because of the small number of conformers for which the TZ data are available. The same applies for the fitting to experimental data, of which the least number was available, both with the ladder C and H models. It led to a fairly large uncertainty for the parameters α_{Si}, β_P, and the components C_1 and C_2 of β_V.

When fitting to the TZ data, besides many physically more or less unreasonable minima, we found what appears to be a continuous series of minima with a growing difference between the parameters β_P and β_R but also a growing error for the orbital energies. A difference between β_P and β_R is expected on qualitative grounds since they reflect the strengths of Si—Si and Si—C bonds, and the latter are about 1.2 times stronger (bond dissociation enthalpies are 382 kJ mol^{-1} for Si—C in SiMe$_4$ and 310 kJ mol^{-1} for Si—Si in Si$_2$Me$_6$[29]). Here,

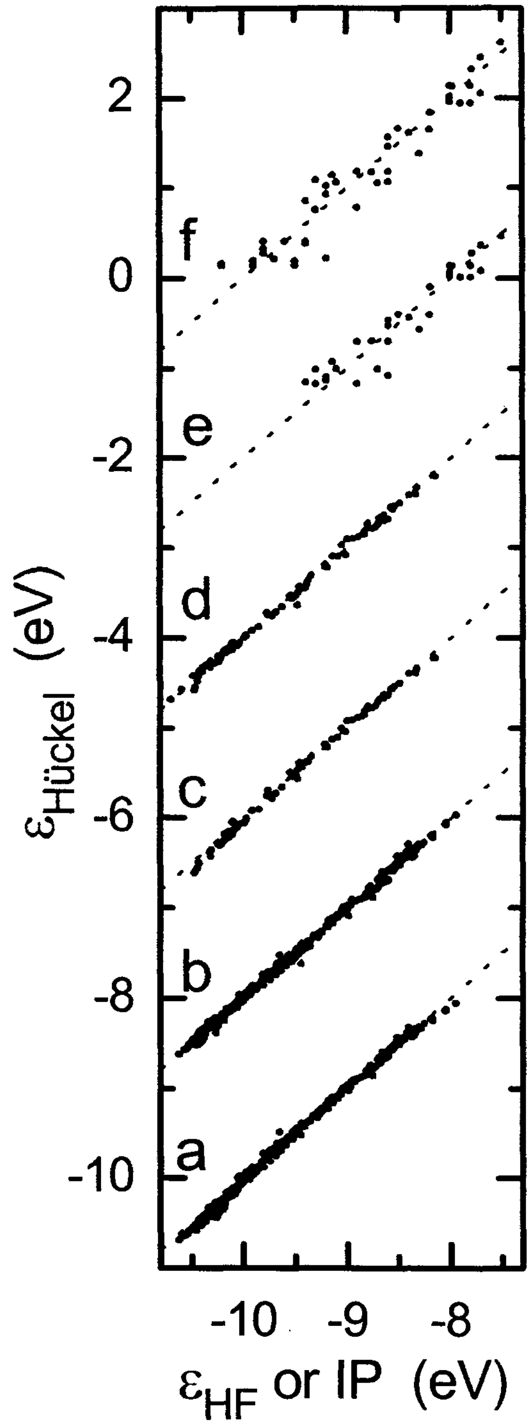

Figure 3. Hückel and HF orbital energies. Optimized ladder C model for (a) DZ and (c) TZ orbital energies and (e) observed IPs. Optimized ladder H model for (b) DZ and (d) TZ orbital energies and (f) observed IPs. Successive plots are displaced vertically by 2 eV

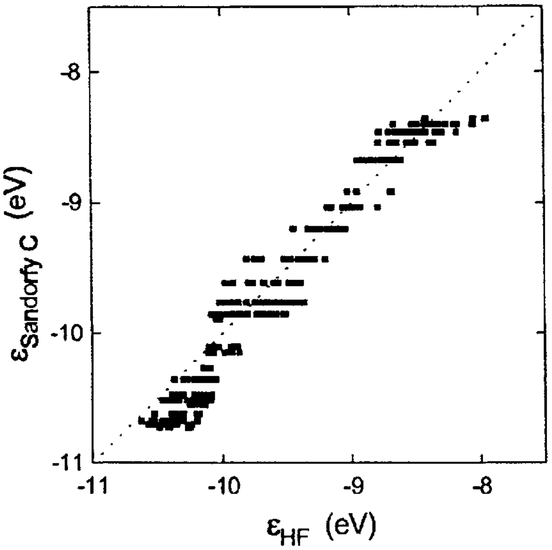

Figure 4. HF DZ and optimized Sandorfy C orbital energies

the uncertainty of the parameters α_S, β_P and the component C_1 of β_V was fairly large. We had no basis for choosing one minimum out of the series other than accommodating this fact and keeping physically reasonable parameter values comparable to those obtained in the fitting to DZ and experimental energies, and the values chosen are therefore somewhat arbitrary. An interpretation of the parameter values cannot go into much detail in these cases.

For comparison, we also optimized parameters in the original Sandorfy C model, in which $\beta_V = 0$ (no conformational dependence).

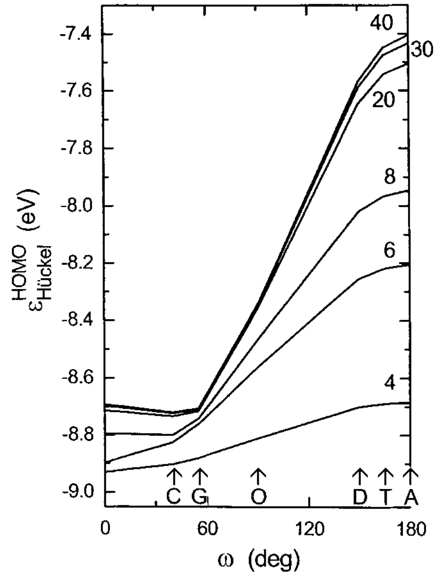

Figure 5. Ladder H (DZ) HOMO energy for Si_4Me_{10}, Si_6Me_{14}, Si_8Me_{18}, $Si_{20}Me_{42}$, $Si_{30}Me_{62}$ and $Si_{40}Me_{82}$, with a uniform dihedral angle ω throughout the backbone

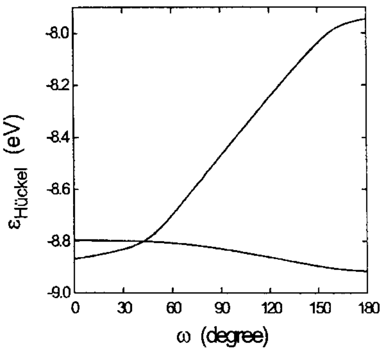

Figure 6. Top two occupied MOs of Si_8Me_{18} in the ladder H model with parameters optimized to DZ data

All final parameter values and the linear regression results for the Hückel vs. the HF orbital energy correlation are given in Table 1. A comparison of orbital energies provided by the *ab initio* method or estimated from experiment using Koopmans' theorem with those obtained from the C and H ladder models with various parameter choices is shown in Fig. 3. A comparison of the orbital energies obtained from the Sandorfy C model with the DZ *ab initio* results is shown in Fig. 4.

HOMO energies in long polysilane chains

We show the results obtained using the Hückel models optimized to the TZ HF orbital energies to predict the HOMO energy in longer chains and its dependence on conformation (the results for parameters optimized to the DZ HF orbital energies were similar). In Fig. 5, the ladder H HOMO energy is shown for several permethylated oligosilanes up to $Si_{40}Me_{82}$, with all dihedral angles ω in the backbone set to the same value between 0 and 180°. Typical ω values for the common conformations of long

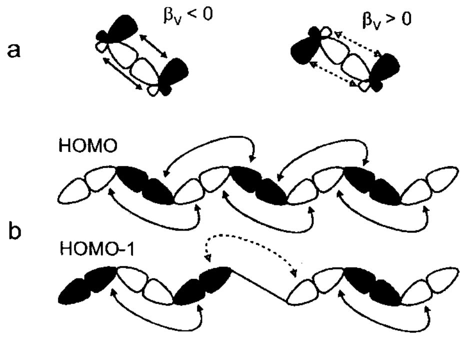

Figure 7. Illustration of (a) the conformational dependence of β_V and (b) the HOMO and HOMO-1 of all-*transoid* Si_8Me_{18} ($\omega = 180°$)

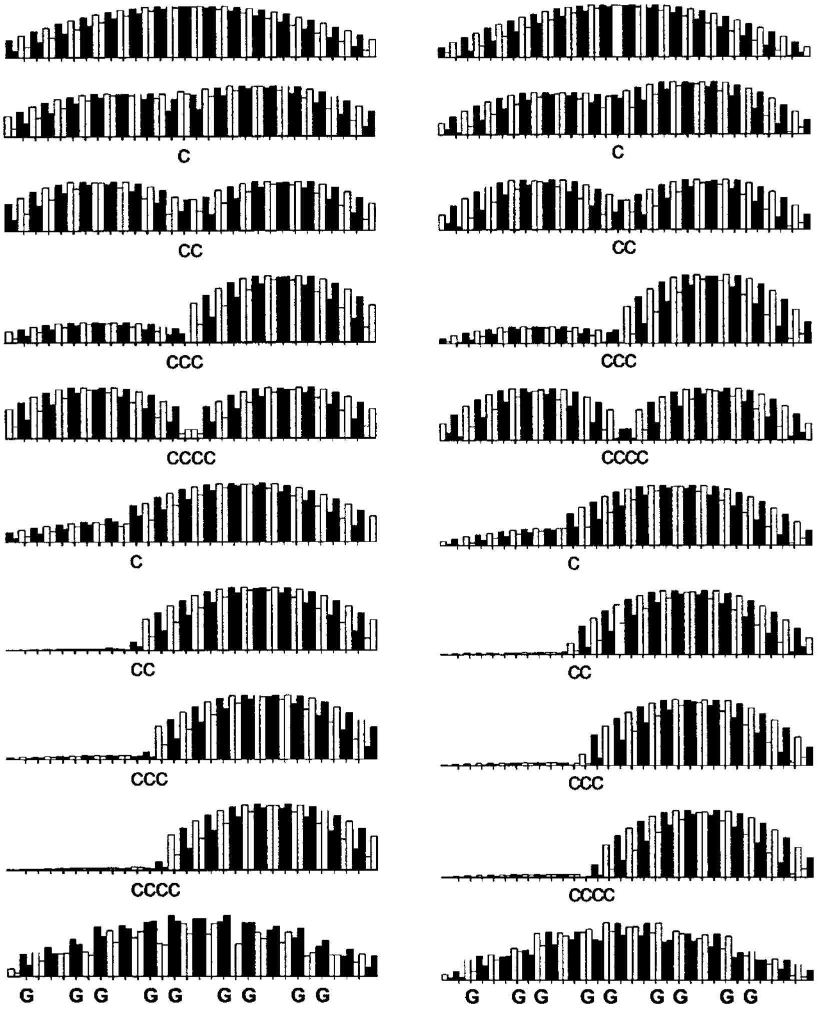

Figure 8. Ladder C (left) and H (right) model (DZ optimized) HOMO coefficients for various conformers of all-*transoid* $Si_{31}Me_{64}$ with *cisoid* links. The amplitude is shown by bar length, the sign by color. Bottom conformer: repeated conformational pattern GT_3GT

polysilane chains[30] are marked by vertical arrows. Results for dihedral angles of less than ~30° are purely hypothetical since steric hindrance prevents the realization of such conformations. The graphs show that the HOMO is generally destabilized as ω increases from the all-*syn* (0°) to the all-*anti* (180°) conformation. The difference between the two is highly dependent on the chain length. For Si_4Me_{10} it is less than 0.2 eV, whereas for $Si_{40}Me_{82}$ it is 1.2 eV. At a chain length of 40, the HOMO energy profile is already nearly converged and longer chains will not have significantly different HOMO energies. The convergence is slowest for conformations with ω close to 180°, where the effects of σ conjugation are most clearly exhibited. For the chains of eight silicon atoms or more, there is a significant change in the HOMO energy profile at ~55°. At dihedral angles ω above this value, the HOMO energy is strongly dependent on ω, whereas it is nearly independent of ω below. This suggests an orbital crossing and a change in the nature of the HOMO. Indeed, ladder H calculations show a crossing of the top two occupied orbitals at a dihedral angle of ~40° in Si_8Me_{18} (Fig. 6). The two orbitals are shown in Fig. 7. In longer chains, a similar crossing occurs, and the orbital whose energy drops as ω is increased crosses a larger number of orbitals whose energy increases. For $Si_{40}Me_{82}$, the calculation predicts a crossing and change in the nature of the HOMO at a dihedral angle of ~55°. The exact location of the crossing points depends on the choice of parameters. *Ab initio* HF orbital energies of Si_8Me_{18} (6–31G* basis set, MMFF94[31] optimized geometries with constrained backbone dihedral angles) behave similarly and show a crossing of the HOMO and the HOMO-1 at a dihedral angle of ~47°.

Polysilane segmentation

The effect of twisted links in an all-*transoid* chain ($\omega = 165°$) on the shape of the HOMO in selected

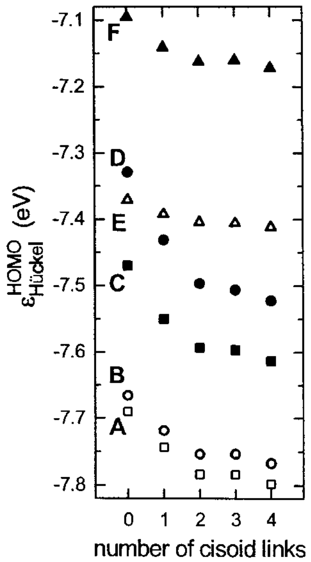

Figure 9. HOMO energy of all-*transoid* $Si_{31}Me_{64}$ with 0–4 *cisoid* links. The *cisoid* links are the 15th (1), the 15th and 16th (2), the 14th, 15th and 16th (3) and the 14th, 15th, 16th and 17th (4) SiSiSiSi dihedral angle in the silicon backbone. Ladder C model parameters optimized to DZ (A) and TZ (B) orbital energies and to observed IPs (E). Ladder H model parameters optimized to DZ (C) and TZ (D) orbital energies and observed IPs (F)

conformers of chains with mostly *transoid* links and one or a few *cisoid* links was studied with the ladder C and ladder H models (Fig. 8). Both yield basically the same results for the amplitude of the MOs in the backbone and lead to the same conclusions about segmentation. The effect of the twisted links on the HOMO energy is shown in Fig. 9. Similar results were obtained for all-*transoid* chains interrupted by one or a few *gauche* links. Predictions for the effect of helicity reversal in an all-*transoid* chain (ω values of 165° and 195°) turned out to be unreliable owing to the great sensitivity of the size and even the sign of the effect to changes of parameter values.

DISCUSSION

Reproducing *ab initio* results

The high degree of coincidence (overlap) between the top half (model C) or quarter (model H) of all the occupied molecular orbitals of the Hückel methods and the *ab initio* orbitals and the excellent correlation of the *ab initio* and Hückel orbital energies (Fig. 3) are remarkable, considering the simplicity of the latter and the very much smaller size of its basis sets. For Si_nMe_{2n+2}, the model H uses a total of $6n + 2$ hybrid orbitals ($4n$ on silicon atoms plus $2n + 2$ on methyl carbon atoms), and the model C uses only $2n - 2$ orbitals on silicon atoms. These numbers can be compared with the $18n + 14$ basis orbitals in the valence part of the natural hybrid orbital space in the *ab initio* description ($4n$ on silicon and $14n + 14$ on methyl groups), and even much larger numbers in the DZ and TZ basis sets.

Clearly, it is the large similarity of all the molecules considered that permits very few parameters to reproduce the key aspects of the results of very complicated calculations. In strictly mathematical terms, we are approximating a few roots of very large Fock matrices, each of whose elements requires elaborate computation, with a few roots of much smaller matrices whose elements have extremely simple functional form, but contain optimized parameters, and this is reminiscent of the interpolation of potential energy surfaces by polynomial roots, known to be very accurate.[32,33]

Comparison of ladder C and ladder H models

Not surprisingly in view of the larger number of adjustable parameters, the ladder H model gave better results than the ladder C model. When evaluating the performance of the simple models, it is important to avoid systematic errors or any peculiar trends in the region of high- or low-lying orbitals that would make their energy deviate significantly from the ideal correlation. This is particularly so for high-energy orbitals, whose properties will affect observable quantities. The ladder H model shows very good slopes close to unity, and the high-lying orbitals do not show significant deviations. In the ladder C model, the slope is slightly worse and the high-lying orbital energies tend to deviate a little. For future use, we recommend ladder H calculations with the DZ parameters. The DZ and TZ ladder C parameter sets are nearly equivalent, and can be used to reduce computational demands for very long chains.

Comparison with the Sandorfy C model

A comparison of the optimized Sandorfy C model with the optimized ladder C model demonstrates the superiority of the latter (Figs 3 and 4). The average error for the orbital energy is 0.16 eV in the former, compared with 0.05 eV in the latter. The difference provides an additional illustration of the effect of chain conformation on the electronic structure of a σ-conjugated system, as all the numerous conformers of a chain at a given length have identical orbital energies in the Sandorfy C model. The considerably larger β_G/β_P ratio in the optimized Sandorfy C relative to the ladder models, similar to those found in earlier work,[16] is easily understood. When β_G and β_V are both introduced in the ladder model, they both contribute to delocalization. The former permits σ conjugation, the latter permits σ hyperconjugation, and for chains with large dihedral angles ω they are synergistic. When β_V is set to zero in the Sandorfy model, the optimization routine tries to compensate for this by artificially increasing the value of β_G relative to β_V, as this now is the only means of enhancing delocalization and improving the fit to the *ab initio* orbital energies.

HOMO energy dependence on conformation

The relation between orbital energies and conformation is the simplest when all backbone dihedral angles in the chain are equal. The increase in the HOMO energy with increasing backbone dihedral angle ω (Fig. 5) reflects the increased delocalization associated with the more positive value of β_V, which acts synergistically with β_G. This is easily understood in terms of first-order perturbation theory[8,21] given the nodal structure of the HOMO (Fig. 8). As ω decreases, β_V is reduced, goes through zero roughly at orthogonal twist (Table 1), and becomes negative at smaller values of ω. Then, its interference with the effects of β_G becomes destructive (σ hyperconjugation cancels some of the σ conjugation) and delocalization, as measured by the energy of the HOMO, decreases considerably. Ultimately, near *gauche* geometry, this orbital is stabilized so much that another molecular orbital becomes the HOMO (Figs 5 and 6). The form of the two orbitals [Fig. 7(b)] makes it clear why one (HOMO at $\omega = 180°$) is greatly destabilized when β_V [Fig. 7(a)] is large and positive (five unfavorable interactions) while the other does not change much (two unfavorable and one favorable interaction).

Polysilane segmentation

Variation of dihedral angles along the backbone introduces the potential for partial localization of orbitals in a chain segment. This was proposed to happen to the HOMO when a *gauche* link is introduced into a long all-*anti* chain,[8] based on semiempirical INDO/S calculations for $Si_{20}H_{42}$. Subsequent HF/STO-3G crystal-orbital calculations[34] disputed this result and concluded that the introduction of *gauche* links does not prevent the delocalization of holes and electrons and does not confine the HOMO (or LUMO) to all-*anti* segments. This result was obtained for infinitely repeated sequences of several anti links separated by a single *gauche* link and the authors attributed the difference in the results to the inadequacies of the semiempirical method. They did not assign the origin of the experimentally observed localization of holes in polysilane chains to any particular conformational feature. Since then, much more has become known about the conformations of permethylated oligosilanes[30] and it seemed of interest to revisit the issue. We now find that one *cisoid* link in a permethylated all-*transoid* chain of 31 silicon atoms localizes the HOMO in the longer part of the chain strongly as originally proposed,[8] and that the amplitude in the shorter part is much lower (Fig. 8). The presence of two or more such links strongly enhances the separation, such that the HOMO amplitude in the shorter part of the chain is entirely negligible. When the chain is divided by twisted links in equal halves, the orbital amplitude is equally distributed over both parts, while the two segments are still well defined. These results support the original proposal[8] that chain segmentation is due to chain twists.

Remarkably, the subsequent *ab initio* results[34] are confirmed by the present results also. As shown at the bottom of Fig. 8, when the *transoid* segments are very short, and the *gauche* links are frequent, the HOMO remains delocalized. Although the present calculation includes the methyl substituent effects and is for an all-*transoid* rather than an all-*anti* chain with added *gauche* links, the result is very similar to that reported earlier[34] for an infinite chain with the same conformational pattern.

We conclude that the difference in the conclusions drawn by the two groups of authors was not due to the difference between two rather approximate methods of calculation, INDO/S[8] and HF/STO-3G,[34] but to the different choice of model systems. It appears that a *cisoid* or a *gauche* link, and more so, two consecutive such links, delimit an all-*transoid* chain segment in which the HOMO is localized, but only if this segment is long enough.

The generally high degree of overlap between the HOMO calculated at the HF/TZ level and those calculated at the ladder C or H model makes it unlikely that the ladder model results of Fig. 8 would be substantially different when calculated with the *ab initio* HF method. A more detailed exploration of the conditions under which the segmentation takes place lies beyond the scope of this paper.

Parameter optimization to experiments

Parameter fitting to the measured ionization potentials yields much worse results than the fitting to *ab initio* results (Fig. 3 and Table 1). The experimental data available for the optimization of the ladder model parameters are rather unsatisfactory for several reasons. To start with, we have to use Koopmans' theorem, which is an exact statement about approximate wavefunctions, to interpret the observed ionization potentials as negative orbital energies. This contributes an only approximately constant shift between the 'experimental' and calculated orbital energies of about 1 eV[10] and thus increases the scatter in the correlation. Furthermore, the ionization potentials are extrapolated from other molecules and not measured on the actual oligosilane conformers they are purported to represent. Some of the spectra are taken on conformer mixtures, believed to be dominated by the all-transoid conformer and therefore interpreted as such. The other spectra were measured on tetrasilanes with additional substituents that constrain the conformation of the silicon chain, but also modify the ionization potentials, as discussed elsewhere.[10] Finally, the observed spectral bands are quite broad and the ionization potentials are only read off with a rather limited accuracy. Taken together, these factors make us favor the parameter values fitted to the *ab initio* results. Even when the objective is a comparison with or a prediction of newly measured ionization potentials, it seems preferable to make ladder C or ladder H predictions based on the parameters fitted to the *ab initio* results, and then apply a constant shift correction as usual when using Koopmans' theorem.

CONCLUSION

We have derived optimized parameters for the ladder C and H models of permethylated polysilanes that reproduce *ab initio* orbital energies of high-lying orbitals with an average error of 0.03 eV and a maximum error of 0.2 eV for the fitted set of conformers. The optimized model permits ionization potential predictions subject to the same Koopmans' uncertainty as *ab initio* Hartree–Fock calculations.

We have discussed conformational effects on HOMO energies and shown that *cisoid* and *gauche* twists in an all-*transoid* chain produce chain segmentation and localization of the HOMO as originally proposed, provided that the segments are long enough. The discrepancies between the results of different authors on this subject have been reconciled.

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