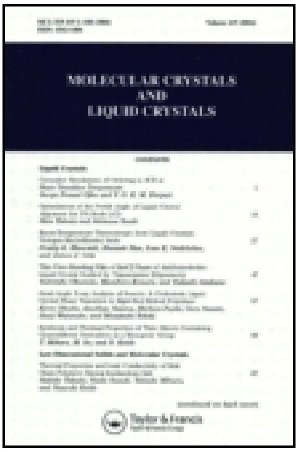

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Electronic States of Linear Tetrasilane and Polysilanes

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ELECTRONIC STATES OF LINEAR TETRASILANE AND POLYSILANES

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Abstract The standard Sandorfy C model of electronic structure of polysilanes is inherently incapable of providing a physical interpretation of the observed conformational effects on UV spectra. We describe a more complicated ladder C model, which still considers only the two backbone hybrid orbitals on each silicon atom, but includes the transfer integrals between all pairs of orbitals on a pair of neighboring silicons. Already at the Hückel level, this model accounts for the general features of the observed spectra both as a function of chain length and of conformation. Results of our *ab initio* calculations suggest, however, that for general non-planar conformations the backbone orbitals should not be treated separately from those that carry the substituents, at least not in relatively short chains. The simplest level at which the conformational effects on the spectra of oligosilanes of all lengths can be accounted for simultaneously will probably be the even more complicated ladder H model, in which all four valence orbitals of each silicon and one orbital of each substituent are considered explicitly.

INTRODUCTION

It has been customary[1] to describe the optical properties of polysilanes in terms of the Sandorfy C model,[2] based on a topological equivalence of a linearly σ-conjugated system of silicon sp^3 hybrid orbitals of a polysilane with a linearly π-conjugated system of carbon $2p$ orbitals of a polyene and thus with a linearly conjugated system of hydrogen $1s$ orbitals in a chain of hydrogen atoms spaced at alternating interatomic distances. At the Hückel level, such a model contains only two parameters, the vicinal transfer integral β_{vic} and the geminal transfer integral β_{gem}. In order to approximate the dependence of the excitation energies of polysilanes on chain length well, the ratio $\beta_{\text{gem}}/\beta_{\text{vic}}$ has to be quite large, on the

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order of 0.5.

In spite of its heuristic utility, this commonly used model of polysilane electronic structure suffers from at least two severe intrinsic problems:

(i) Since by definition, the values of β_{vic} and β_{gem} are invariant to pure rotation around the SiSi bonds, the model predicts identical spectra for all conformers of a given chain length. This is true not only at the Hückel level, but also at the Hubbard and extended Hubbard levels of theory. Yet, it has been clear for some time that the optical properties of polysilanes are a quite sensitive function of chain conformation.[3] The recent separate determination[4] of the excitation energies of the first intense transitions of the gauche and anti conformers of Si_4Me_{10}, which differ by 3/4 eV, are particularly instructive in this regard. Indeed, the excitation energy of the gauche conformer of Si_4Me_{10} is even a little higher than that of Si_3Me_8!

Although at the PPP level of the Sandorfy C model the predicted spectra of conformers of identical chain length are no longer exactly the same, the observed differences still cannot be accounted for. Although it is possible in principle to fit the results for various conformers by postulating a different β_{gem}/β_{vic} ratio for each, this is clearly unphysical.

(ii) The transition energy decrease predicted by the model upon going from Si_2Me_6 to Si_3Me_8 is considerably larger than that predicted for going from Si_3Me_8 to Si_4Me_{10}, regardless of the value chosen for the β_{gem}/β_{vic} ratio. Experimentally, the two are about the same. After the values of β_{gem} and β_{vic} have been adjusted so as to reproduce the excitation energies of Si_2Me_6 and of an infinitely long chain, the plot of the predicted excitation energy against chain length for the all-anti conformers decreases too fast at first and not fast enough for the longer chains.[5]

An additional concern is the total neglect of orbitals that are not needed to describe the SiSi bonding in the backbone at the lowest level of approximation and are only needed to describe the bonds that carry the chain substituents (i.e., the use of Sandorfy C as opposed to H approximation). Is this really acceptable for general SiSiSiSi dihedral angles?

For angles of 180° (anti) and 0° (syn), all of the Si atoms lie in a plane of symmetry, molecular orbitals can be classified as σ or π, and low-energy excited states can be classified as $\sigma\sigma^*$ or $\sigma\pi^*$. The Sandorfy C model only permits the description of σ orbitals and $\sigma\sigma^*$ states. Prior *ab initio* calculations[6] suggest that the lowest $\sigma\sigma^*$ state will lie at a lower energy than the lowest $\sigma\pi^*$ state in all all-anti Si_nH_{2n+2} chains except for the very shortest two or three, and one hopes that peralkylation will not change the situation. In the spectra of the longer chains, the presumably very weak transitions into the $\sigma\pi^*$ states are then generally assumed to be present at higher energies, similarly as transitions into Rydberg states. Both are believed to be inobservable due to overlap with the much stronger $\sigma\sigma^*$ transitions. Little if any attention has been paid to the dihedral angle of 0°, since it is not physically possible to attain an all-syn geometry in a long chain, due to excluded volume effects. A syn geometry can be reached only in Si_4Me_{10}, and probably does not correspond to a minimum in its ground state surface.

Although this rationalization of the qualitative success of the Sandorfy C model in the interpretation of the absorption spectra of all-anti oligosilanes and polysilanes is appealing, and probably correct, it is not obvious that it applies to conformers with other dihedral angles, particularly those whose lower symmetry does not prevent the mixing of would-be $\sigma\sigma^*$ states, present in the model, with would-be $\sigma\pi^*$ states, absent in the model. Even if such mixing were to be unimportant for long chains, where the $\sigma\sigma^*$ configurations might well be below the $\sigma\pi^*$ configurations at all important geometries, it could still be important for short chains, and might thwart attempts to derive parameter values by fitting the spectra of individual conformers of short chains, which have now started to become available.[4,5] If a model, such as Sandorfy C, does not permit an explicit treatment of $\sigma\pi^*$ states, since it is limited to SiSi backbone orbitals, it may be necessary to correct the derived parameter values for the effects of σ-π mixing in those conformers that are not all-anti.

The problems (i) and (ii) are neatly solved by the recently proposed "ladder C" model for the electronic structure of σ conjugated polymers,[4,5] which we shall briefly describe in the following. We used the spectra of individual conformers of relatively short chains to calibrate this model, and the agreement with experiment was impressive already at the Hückel level.[5] Unfortunately, we now must report that the hint of severe distortions due to σ-π mixing, provided by *ab initio* calculations for Si_4H_{10} and reported at a recent conference,[7] has survived further scrutiny: it now appears that the agreement with experiment that resulted from the parameter fitting procedure was fortuitous. There still is a good chance that a differently calibrated ladder C model will be adequate for the description of the spectroscopy of long polysilanes, but for short ones, an explicit consideration of σ - π interactions appears unavoidable. For these, and possibly even for the long ones, we need to include explicitly all four sp^3 hybrids on each Si atom, and an orbital of each substituent. This will result in the considerably more complicated "ladder H" model.

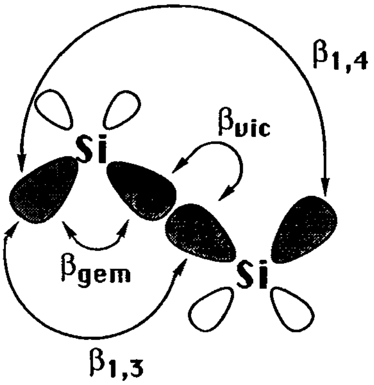

FIGURE 1 Transfer integrals between sp^3 hybrids in an oligosilane.

THE LADDER C MODEL OF σ CONJUGATION

The ladder C model[4,5] is a generalization of the classical Sandorfy C model. It uses the same basis set of two sp^3 hybrids on each Si atom to represent the SiSi backbone (Fig. 1), but in addition to the transfer integrals β_{gem} between neighboring hybrids located at the same Si atom, and β_{vic} between hybrids pointing at each other from neighboring Si atoms, it also considers the other two transfer integrals $\beta_{1,3}$ and $\beta_{1,4}(\omega)$ between the two hybrids located on neighboring Si atoms (ω is the dihedral angle).

Very similar a priori estimates of the relative magnitudes of the four transfer integrals have been obtained in two ways:[5] (i) from consideration of their values in extended Hückel theory, i.e. from expectations for non-orthogonal hybrids built from atomic Slater orbitals, and (ii) from Hartree-Fock matrix elements in the basis of natural hybrid orbitals[8] (Fig. 2). Numerical estimates were obtained from fits to experimental data.[5]

All estimates indicate that $\beta_{1,3}$ is significantly smaller than the other two transfer integrals that are insensitive to conformation, β_{vic} and β_{gem}. Thus, it may be possible to minimize the number of adjustable parameters by setting it equal to zero, in the hope that its effects can be incorporated in the values of β_{vic} and β_{gem}. Success in this regard is not guaranteed, since the presence of $\beta_{1,3}$ will cause a removal of alternant symmetry, and this may but need not be required to fit the experimental data. For the time being, we have set $\beta_{1,3}$ equal to zero, since this was suggested as optimal by all atempts to fit the observed excitation energies.

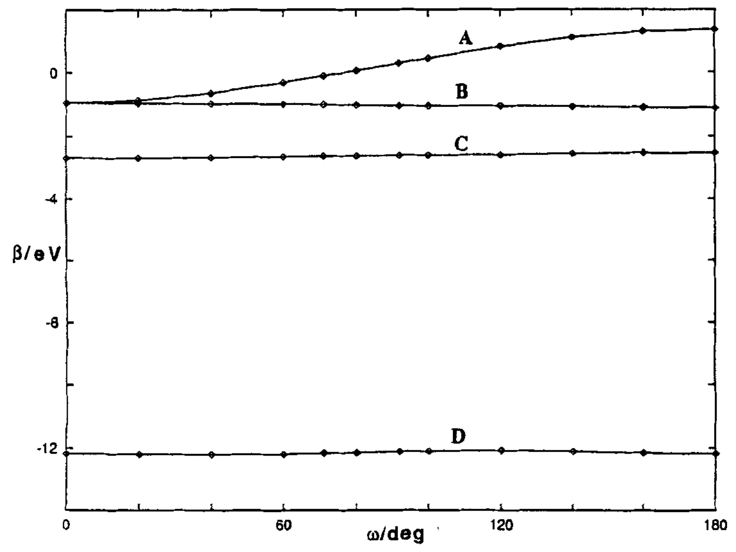

FIGURE 2 Hartree-Fock matrix elements between natural hybrid orbitals in the silicon backbone of tetrasilane in a 3-21G* basis set: $\beta_{1,4}(\omega)$ (A), $\beta_{1,3}$ (B), β_{gem} (C), β_{vic} (D).

The transfer integral $\beta_{1,4}(\omega)$ is the only one of the four that depends on the dihedral angle ω defined by rotation about the bond connecting the two Si atoms. Its presence permits the description of conformational effects on the electronic structure. The mutual orientation of the two hybrids involved is intermediate between σ and π, and because of the presence of the π component in their overlap, the integral $\beta_{1,4}(\omega)$ changes from negative to positive as the dihedral angle ω changes from 0° (syn) to 180° (anti), going through zero somewhere in the vicinity of 90°. At 0° and 180°, the magnitude of $\beta_{1,4}(\omega)$ is estimated to be within a factor of two of β_{gem} in absolute value, and this, in turn, is about six times smaller than β_{vic}. This is physically much more reasonable than the situation in the simple Sandorfy C model, where β_{gem} needs to be about half the size of β_{vic} in order to fit the observed decrease of excitation energy with increasing chain length. In the Sandorfy C model β_{gem} is the only transfer integral present that provides for conjugation between otherwise isolated SiSi bonds, and its value therefore needs to be exaggerated to fit the observed red shift caused by conjugation, even approximately. In the ladder C model, this role is shared between β_{gem} and $\beta_{1,4}(\omega)$, and each can have the relative value expected a priori from hybrid orbital properties.

In the ladder C model with β_{gem} set equal to zero, the topology of the interaction of the basis set orbitals is no longer linear as in the Sandorfy C model, but resembles a ladder (Fig. 3). The two side pieces consist of alternating β_{vic} and $\beta_{1,4}(\omega)$ integrals, and the rungs consist of β_{gem} integrals. The orbital energy changes from Si_2Me_6 to Si_3Me_8 are due strictly to rung conjugation (β_{gem}), and it is only in Si_4Me_{10} that side-piece conjugation [$\beta_{1,4}(\omega)$] sets in. This provides a natural rationale for the otherwise disproportionately small excitation energy drop from Si_2Me_6 to Si_3Me_8, and thus for point (ii) above.

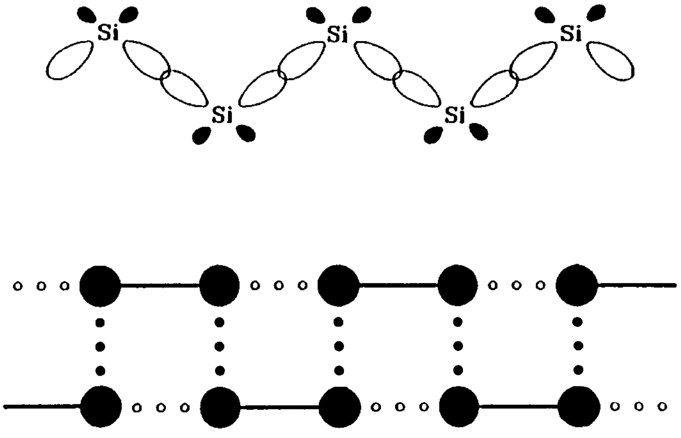

FIGURE 3 The topology of orbital interaction in an oligosilane backbone (with the two sp^3 orbitals on each Si placed above each other): full lines, β_{vic}; dotted lines, β_{gem}; lines of empty circles, $\beta_{1,4}(\omega)$.

An explanation of the conformational effects, above point (i), is now also straightforward. Instead of dealing with a linear system, in which interruption of conjugation between SiSi bonds consists of the removal of a single transfer integral β_{gem} and thus inevitably increases the excitation energy, we are now dealing with a system with interacting conjugation paths that interfere coherently. Interruption of conjugation corresponds to the removal of one β_{gem} and two $\beta_{1,4}(\omega)$ interactions, and the removals can interfere in a destructive or a constructive fashion, depending on the signs of the two $\beta_{1,4}(\omega)$ integrals, as is easily rationalized in terms of first-order perturbation theory. Since the signs, in turn, are dictated by the dihedral angles, it is obvious how conformational dependence of the optical properties results, and how the effect of chain extension on the transition energy can range from large to zero, depending on conformation. This has been discussed in some detail elsewhere.[5]

The observation of a large red shift of the first intense transition in Si_3Me_8 upon extending the chain by one silicon in the anti fashion, and no red shift upon extending it in the gauche fashion[4] provided a basis for finding a set of parameters by a non-linear least squares fit to all available observed excitation energies. This permitted the ladder model to account for the data for all the known conformers of permethylated chains of up to five Si atoms quantitatively.[5] In eV, and setting $\beta_{1,3} = 0$, the parameters are $\beta_{vic} = -3.32$, $\beta_{gem} = -0.62$, $\beta_{1,4}(\text{anti}) = +0.75$, $\beta_{1,4}(\text{gauche}) = -0.40$. At this point we felt that a relatively simple parameterized description of polysilane one-photon absorption spectra for all conformers was within reach (Fig. 4).

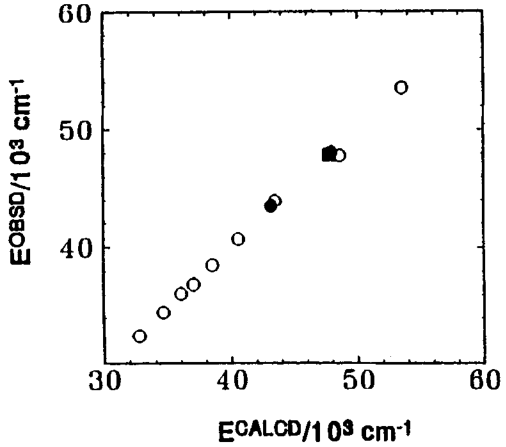

FIGURE 4 The ladder C model: observed and calculated $\sigma\sigma^*$ excitation energies of permethylated oligosilanes. Open points, all-anti conformers; dark points, other conformers.

However, three observations made us doubt the validity of the fit. First, preliminary data for the individual conformers of Si_6Me_{14} were not accounted for well. Second, even the best *ab initio* calculations we were able to perform did not fit the experiment, in that the calculated lowest excitation energy differences among the conformers were far smaller than observed. Third, although most of the parameter values were just those anticipated from Fig. 2, the value of $\beta_{1,4}$(gauche) required to fit the data seemed to be quite strongly negative, while a value near zero would have been expected for a dihedral angle close to 92°, predicted[4] at the HF level for the gauche conformer of Si_4Me_{10} (0.9 kcal/mol above the anti minimum, located at a dihedral angle of 162°; a single-point MP2 calculation reduces the difference to 0.8 kcal/mol). The situation has since become more complicated in that we have now found another very slightly more stable gauche minimum for Si_4Me_{10} at the HF level of calculation (0.7 kcal/mol above the anti conformer, reduced to 0.1 kcal/mol at the MP2 level), at a dihedral angle of 54° (Fig. 5). If this is the correct angle in the conformer for which the observations have been made, the discrepancy between the anticipated value of $\beta_{1,4}$(gauche) and the value that resulted from the least squares fit is far less serious. It should be noted that the first reported calculation that predicted the existence of two distinct gauche conformers of permethylated oligosilanes, with different dihedral angles, was performed some time ago using the MNDO/2

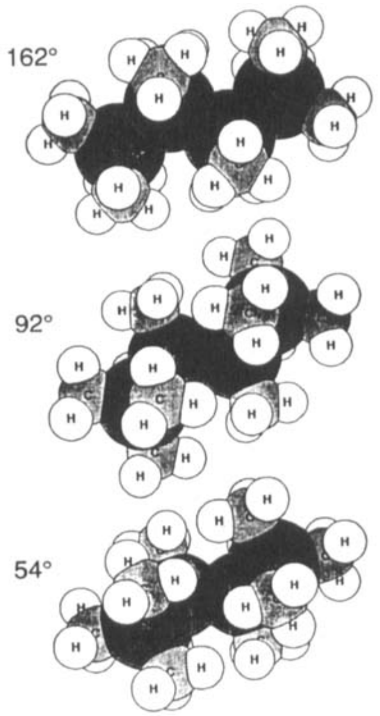

FIGURE 5 The three conformers of Si_4Me_{10} obtained at the Hartree-Fock level of calculation (3-21G* basis set), with the dihedral angles.

method.[9] The energy differences and the barriers between the minima are very small and we are still unsure of their significance. We are presently attempting to resolve the issue by a combination of additional experiments with a higher level of calculation.

Regardless of the outcome of our efforts to establish the dihedral angle in the observed gauche conformer or conformers of Si_4Me_{10}, the fact remains that the doubts that were triggered by the initial observations prompted us to perform a series of calculations described in the following section, and that these suggest very strongly that the excellent fit found earlier[5] for the ladder C model at the Hückel level (Fig. 4) was fortuitous. We now believe that we are quite far from being able to describe all polysilane conformers with a parameterized ladder C model.

EXCITED STATES OF TETRASILANE AS A FUNCTION OF THE DIHEDRAL ANGLE

Figure 6 shows the excitation energies of Si_4H_{10} for dihedral angles ranging from 0° (syn) to 180° (anti), calculated at the all-singles CI level with the 6-31G** basis set. Figure 7 shows the corresponding oscillator strengths at the lame level of calculation. These results are similar to the preliminary results obtained previously with more limited CI and reported recently at a conference.[7]

The results indicate that Si_4H_{10} actually has four low-lying excited singlet states, and we suspect that the situation in Si_4Me_{10} will be similar. Two of the states (A) are symmetric with respect to rotation around the two-fold axis of

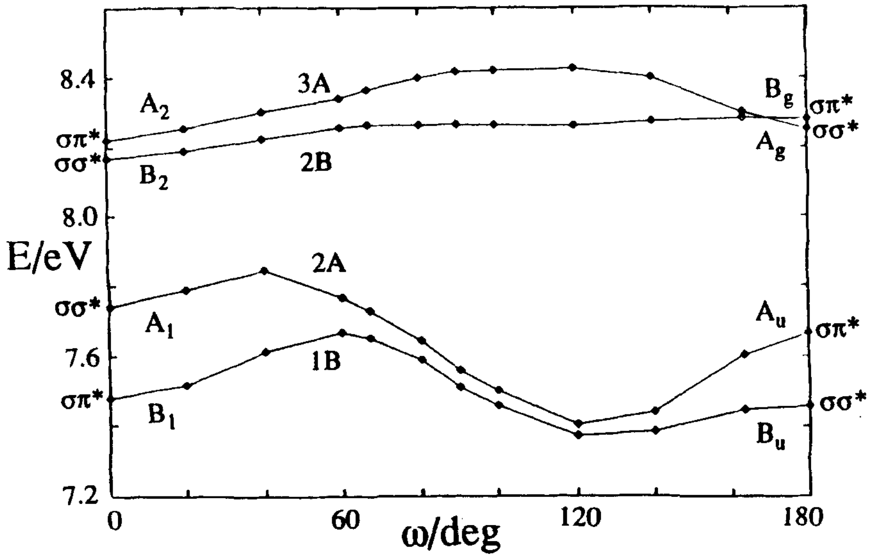

FIGURE 6 6-31G** excitation energies of the low-energy valence transitions of Si_4H_{10} as a function of the dihedral angle ω.

symmetry that is preserved at all dihedral angles. Transitions into them are calculated to be very weak at all dihedral angles, and are not likely to be observable in ordinary absorption spectra. At the two high-symmetry geometries, anti ($\omega = 180°$) and syn ($\omega = 0°$), one of these states is of the $\sigma\sigma^*$ type and the other of the $\sigma\pi^*$ type. Their very low intensities are easy to understand qualitatively, since in both cases the excited state wavefunction is derived from the ground state determinant by a single electron promotion that introduces more than a single new nodal surface. E.g., the $\sigma\sigma^*$ excitation into an A state promotes an electron from the second highest occupied molecular orbital (MO) of σ symmetry to the lowest unoccupied MO of σ symmetry, the node numbers differ by two, and the transition is likely to be intense in a two-electron but not a one-electron absorption spectrum. We dismiss the A states from further consideration in the present context.

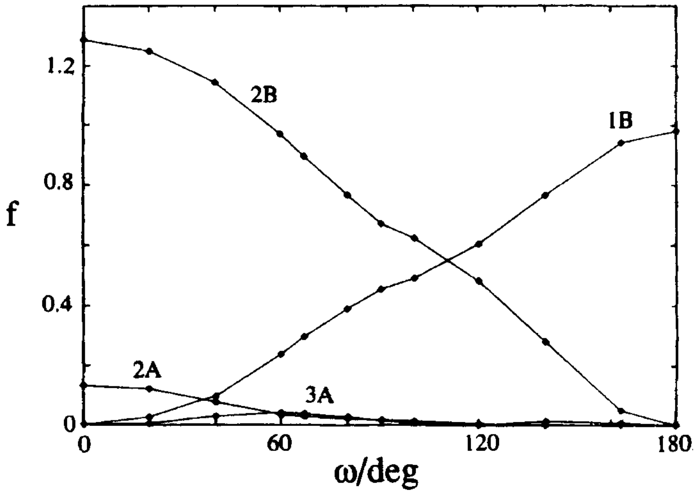

FIGURE 7 6-31G** oscillator strengths of the low-energy valence transitions of Si_4H_{10} as a function of the dihedral angle ω.

The other two states (B) are antisymmetric with respect to rotation around the symmetry axis. One of these is of the $\sigma\sigma^*$ type in both the syn and the anti high-symmetry limit, and has very high intensity. In both cases, it corresponds to a single electron promotion from the highest occupied MO of σ symmetry to the lowest unoccupied MO of σ symmetry. Their node numbers differ by one, and the high intensity is readily understandable. This is exactly the transition that is being described by the simple models such as Sandorfy C or ladder C.

The other state of B symmetry is of the $\sigma\pi^*$ type in both the syn and the anti limit, and has nearly zero calculated intensity. Again, this is understandable in qualitative terms since the transition can be described as a one-electron promotion between orbitals whose node numbers differ by more than one. The standard procedure of dismissing $\sigma\pi^*$ states as inobservably weak in the spectra of oligosilanes would thus once more appear to be vindicated, and the association of the only transition calculated at the *ab initio* level as intense and observable with the $\sigma\sigma^*$ transition of the simple models would appear to be justified. The ladder C model should have a good chance to work at the syn and anti geometries.

However, for conformations other than anti or syn, the symmetry element that distinguishes between σ and π symmetry is absent, and the two configurations of B symmetry must be expected to mix. If they were well separated in energy, the effects of such mixing would most likely be negligible, and this may well be the case in oligosilanes with long chains. In Si_4H_{10}, the $\sigma\sigma^*$ configuration is the lower of the two at the anti geometry, and the higher at the syn geometry, and an avoided crossing results. At intermediate values of the dihedral angle ω, the configurations inevitably will mix strongly, and two states of mixed $\sigma\sigma^*$ - $\sigma\pi^*$ nature will result. The two transitions will then share the intensity that would otherwise be expected for the $\sigma\sigma^*$ transition alone. Near the anti limit, the lower transition will be approximately $\sigma\sigma^*$ and the more intense. Near the syn limit, the upper transition will be approximately $\sigma\sigma^*$ and the more intense, but neither one will change its energy much as a function of ω (Figs. 6 and 7).

These results suggest that the large blue shift of the absorption peak observed upon going from the anti to the gauche conformer[4] is only partly due to an increase in the energy of a diabatic $\sigma\sigma^*$ conformation, and is partly due to σ - π interaction, which displaces the 2B state in Fig. 6 to higher energies, and the 1B state to lower energies in the region of the avoided crossing. It is therefore not correct to use the observed energy of the gauche conformer to calibrate a model that does not incorporate MOs of π symmetry, such as ladder C. In effect, the parameter value for $\beta_{1,4}$(gauche) derived from our least squares fitting corresponds to the syn and not the gauche conformation, since that is the conformation at which the observed transition energy corresponds to a pure $\sigma\sigma^*$ excitation if we believe Fig. 6.

The correct value of experimental gauche excitation energy to use in the fitting procedure would be lower than that observed, and this would affect the resulting parameter values. The model would then predict transition energies as they would be in the absence of σ - π interactions, and for those short chains in which such intraction is important, e.g., Si_4H_{10}, it would disagree with observations. However, if the σ - π interactions are negligible in long polysilanes, the model would give good predictions for them. We are currently attempting to develop and test such a set of parameters for the ladder C model.

An alternative is to expand the model basis set to include all four sp^3 hybrids on each silicon and an orbital on each substituent (ladder model H), and to attempt to find a set of parameters that reproduces the behavior displayed in Figs. 6 and 7. Such a model would be substantially more complicated, but could potentially work for oligosilanes of all lengths.

CONCLUSIONS

The Sandorfy C model should be abandoned whenever the conformational dependence of the properties of polysilanes is of interest, and offers no advantages over the ladder C model even in the case of all-anti conformers. The ladder C model may be capable of reproducing correctly the observed transition energies in long-chain oligosilanes, including their conformational dependence, but not in the short ones, because in these, σ - π interactions are important. In order to reproduce correctly the conformational dependence of transition energies in chains of all lengths, one needs to go at least to the ladder H model, and possibly beyond.

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REFERENCES

1. L. A. Harrah and J. M. Zeigler, in Photophysics of Polymers, ACS Symp. Ser. 358, edited by C. E. Hoyle and J. M. Torkelson (American Chemical Society, Washington, DC, 1987), p. 127; M. J. Rice and S. R. Philpott, Phys. Rev. Lett., 58, 937 (1987); U. Rauscher, J. Bässler and R. Taylor, Chem. Phys. Lett., 162, 127 (1989); C. Walsh, D. M. Burland and R. D. Miller, Chem. Phys. Lett., 175, 197 (1990); A. Herman, B. Dreczewski and W. Wojnowski, Chem. Phys., 98, 475 (1985); A. Herman, Chem. Phys., 122, 53 (1988); Z. G. Soos and G. W. Hayden, Chem. Phys., 143, 199 (1990); S. Bloński, A. Herman and S. Konieczny, Spectrochim. Acta, Part 1, 45, 753 (1989); Z. G. Soos and R. G. Kepler, Phys. Rev. B, 43, 11908 (1991); R. G. Kepler and Z. G. Soos, Phys. Rev. B, 43, 12530 (1991).

2. C. Sandorfy, Can. J. Chem., 33, 1337 (1955).

3. R. D. Miller and J. Michl, Chem. Rev., 89, 1359 (1989).

4. H. S. Plitt and J. Michl, Chem. Phys. Lett., 198, 400 (1992).

5. H. S. Plitt, J. W. Downing, M. K. Raymond, V. Balaji, and J. Michl, J. Chem. Soc. Faraday Trans., 90, (1994), in press.

6. V. Balaji and J. Michl, Polyhedron, 10, 1265 (1991).

7. H. S. Plitt, J. W. Downing, H. Teramae, M. K. Raymond, and J. Michl, presented at the International Symposium on Polymers for Microelectronics in Japan, November 1993, ACS Symp. Ser., edited by S. Ito, S. Tagawa, and K. Horie (American Chemical Society, Washington, DC, in press).

8. A. E. Reed, L. A. Curtiss, and F. Weinhold, Chem. Rev., 88, 899 (1988).

9. W. J. Welsh, W. D. Johnson, Macromolecules, 23, 1882 (1990).