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A Force Field (MM2) Study of 1,2-Di-*tert*-butyl- and 1,2-Disilylcyclohexanes

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The results of empirical force field calculations (MM2-82) on conformers of the cis and trans isomers of 1,2-disilylcyclohexane (DSC), 1,2-bis(trimethylsilyl)cyclohexane (BTMSC), and 1,2-bis(trimethylsilyl)cyclohexenes (BTMSCE) are reported. The calculations use several force field parameters which have been developed recently. We compare the energy differences of the aforementioned with 1,2-di-*tert*-butylcyclohexanes (DTBC) and 1,2-dimethylcyclohexanes (DMC), and we find in 1,2-bis(trimethylsilyl)cyclohexane, as in the *trans*-1,2-di-*tert*-butylcyclohexane system, a substantial population of a diaxial conformation. We report ab initio calculations on propylsilane, silylcyclohexane, 1,2-disilylcyclohexane, methylcyclohexane, and 1,2-dimethylcyclohexane, which were useful in calibrating additional MM2 parameters and evaluating the validity of those previously developed by Frierson, which we used in our studies of silanes. These calculations, including full geometry optimizations as possible, were performed at the 3-21G(*) and 3-21G levels mainly, with MP3/3-21G(*)//3-21G(*) and 3-21G(*)//MM2 calculations performed as appropriate.

Introduction

Molecular mechanics calculations have been successfully applied to a variety of cyclic silanes.[1,2] The procedure gives very good reproduction of structural parameters for even moderately strained silanes (e.g. silacyclopent-3-ene). Our research in organosilicon chemistry over the past decade has emphasized the use of cyclic silanes as systems in which to study details of reaction pathways. In connection with that work, we have been particularly interested in developing reliable means of predicting conformational properties of cyclic silanes as an adjunct to our research on conformational and other stereochemical effects on reactivity. The particular studies reported here were initiated as a result of correspondence with Professor William Kitching (University of Queensland, Australia) concerning conformational preferences of silyl-substituted cyclohexanes. He has experimentally determined an *A* value for the trimethylsilyl group (2.5 ± 0.1 kcal/mol)[3] attached to the cyclohexane ring and has also reported NMR studies of bis(trimethylsilyl)cyclohexanes (BTMSC).[4]

The steric bulk of trimethylsilyl groups, particularly when attached to adjacent carbons of the cyclohexane ring, could impart substantial deformations of the usually preferred chair cyclohexane conformations. A less expected alternative would be that one or both of these bulky groups might adopt an axial conformation. The modeling of bis(trimethylsilyl)cyclohexanes presents an interesting challenge to the empirical force field method. Van de Graaf, et al. have examined previously the 1,2-di-*tert*-butylcyclohexane (DTBC) system by force field methods in studies addressing similar questions with respect to this hydrocarbon.[5] Their calculated conformational energies and heat of formation were in good agreement with conclusions based on a variety of experimental data.

The magnitude of the *A* value for $SiMe_3$ reported by Kitching is substantially lower than that for *tert*-butyl (5.4 kcal/mol),[6] and we wished to determine by computational means whether this difference leads to unexpected conformational behavior in BTMSC.

In our initial studies of 1,2-bis(trimethylsilyl)cyclohexane using the standard MM2 force field (MM2-77), we found the trans diaxial orientation to be an energy minimum.

Table I. Relative Steric Energies of 1,2-Disubstituted Cyclohexanes/Cyclohexenes from MM2 Calculations

compd	cis e,a	trans a,a	trans e,e	trans twist[a]
BTMSC	1.800	0.000	1.700	2.340
DTBC	5.270	0.000	6.730	0.390
DSC	0.780	0.690	0.000	5.800
DMC	1.614	2.434	0.000	6.400
BTMSCE	4.590	0.000	2.200	

[a] Only the lowest energy twist form is considered.

This result prompted us to explore the conformational behavior of 1,2-disilylethane (DSB) as a model of the Si–C–C–Si fragment. We refer the reader to an earlier paper detailing this work.[7] Any parameters required to study the BTMSC system that were not part of the recently developed MM2 force field for silanes[1] have been developed by us, including the C=C–C–Si fragment in the silylcyclohexenes.[8]

After developing force field parameters appropriate for the 1,2-disilylethane system, we now report results for BTMSC, BTMSCE, and DSC. A long endocyclic (Si)C–C(Si) zero-energy bond length, as detailed previously for 1,2-disilylethane, was used in the calculations (1.563 Å, which is the usual value plus 0.04 Å as polarization correction). The calculations were performed in a stepwise manner, first by substituting three methyl groups on one silicon, minimizing the structure, and then adding three more methyl groups on the other silicon atom. This facilitates energy optimization for each conformer.

In addition, subsequent to the completion[9] of the bulk of the work reported herein, we have performed ab initio

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(1) Frierson, M. Ph.D. Dissertation, University of Georgia, 1984.

(2) (a) Allinger, N. L.; Tribble, M. T. *Tetrahedron* 1972, *28*, 2147-2156. (b) Cartledge, F. K. *J. Organomet. Chem.* 1982, *225*, 131-139. (c) Mislow, K.; Stackhouse, J.; Hummel, J. P. *Tetrahedron* 1977, *33*, 1925-1930.

(3) Kitching, W.; Olszowy, A. H.; Drew, M. G.; Adcock, W. *J. Org. Chem.* 1982, *47*, 5153-5156.

(4) Wickham, G.; Kitching, W. *Organometallics* 1983, *2*, 541-547.

(5) Van de Graaf, B.; Van Belkum, H.; Van Koningsveld, H.; Sinnema, A.; Van Veen, A.; Wepster, R. M.; Van Wijk, M. A. *Recl. Trav. Chim. Pays-Bas.* 1974, *135*, 93-99.

(6) Allinger, N. L. *J. Am. Chem. Soc.* 1977, *99*, 8177; MM2-77 (QCPE No. 395).

(7) Profeta, S., Jr.; Unwalla, R. J.; Nguyen, T. B.; Cartledge, F. K. *J. Comput. Chem.* 1985, *4*, 528-538.

(8) Profeta, S., Jr.; Unwalla, R. J.; Cartledge, F. K. *J. Org. Chem.* 1986, *51*, 1884-1885.

(9) Unwalla, R. J. Ph.D. Dissertation, Louisiana State University, 1986.

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calculations on several systems including propylsilane, methylcyclohexane, silylcyclohexane, DSC, and DMC to provide further insights into the conformational energies of these models. Further, we have rerun the previously reported[9] silane calculations using the full MM2-82 parameter set,[10] augmented by our values as detailed previously[7] and herein (a complete list of Si-containing parameters used in this work is in the appendix).

Results and Discussion

BTMSC and DTBC. A synopsis of energies for the conformers of BTMSC and DTBC as calculated by MM2 is shown in Table I. An examination of MM2 steric energy components of the BTMSC conformers shows the diaxial conformer having the lowest energy. The relative energy of the trans diequatorial conformer and the cis isomer are 1.70 and 1.80 kcal/mol, respectively. Calculations were done on several twist forms, those for the most stable are listed in Table I. The relative energy of this twist form is 2.34 kcal/mol. The calculated structure of the diaxial conformer reflects the tendency of the axial trimethylsilyl groups to avoid severe nonbonded interactions with the other atoms of the molecule. This results in a decrease in the Si–C–C–Si dihedral angle (140.2°) and some flattening of the ring.

We compared this result with those for the hydrocarbon analogue, 1,2-di-*tert*-butylcyclohexane (DTBC). Van de Graaf[5] reported calculations on this system using early force fields of Allinger (MMI) and Schleyer (EAS). We report these calculations using MM2-77,[6] which, particularly in the case of hydrocarbons, should yield more accurate relative energy differences due to its improved torsional potentials and a more balanced treatment of the nonbonded interactions. The results are not strikingly different from those published earlier except that the relative energy values of the strained conformations are somewhat smaller (i.e., trans (ax,ax) – trans (eq,eq) = 6.7 kcal/mol compared to 7.8 kcal/mol[5] (Table I)). An examination of the values for dihedral angles of BTMSC and DTBC clearly shows that despite the differences between the *tert*-butyl and trimethylsilyl groups in terms of bond lengths, their impact on the cyclohexane group is quite similar. A synopsis of the calculated trends in the conformational behavior of BTMSC and DTBC is as follows:

(a) In the BTMSC case, the trans diaxial conformation is substantially stabilized, while DTBC exists as a mixture of the trans diaxial and twist forms.

(b) In both systems bending energy is at a minimum in the twist conformer while torsional energy is at a maximum.

(c) In BTMSC the relative energy of a cis isomer is also smaller (1.8 kcal/mol) than that found in DTBC (5.27 kcal/mol).

(d) In BTMSC, the ax–ax/eq–eq trans conformer energy difference is much smaller (1.7 kcal/mol) relative to DTBC (6.76 kcal/mol).

(e) The compression, bending, torsional, and van der Waals energies in the hydrocarbon system are substantially greater, on a conformer by conformer comparison, than in the BTMSC system. In addition, the attractive nonbonded interactions of the Me_3Si groups dominate in the BTMSC system while repulsive interactions of the *tert*-butyl groups are dominant in the hydrocarbon.

The majority of the above findings can be rationalized in the following way. In the BTMSC trans diequatorial conformer as well as the cis isomer there are not only reduced nonbonded repulsive interactions but also substantial attraction between the trimethylsilyl groups. These attractive interactions may arise from longer Si–C bond lengths and methyl/methyl distances and enhanced silicon/methyl attractions. The relatively long C–C bond length (1.563 Å) between the two Si–C bonds places the Me_3Si groups farther away from each other. However, in the diequatorial or ax–eq DTBC cases, due to the shorter C–C bonds, repulsive nonbonded interactions dominate. As the axial *tert*-butyl groups retreat from the repulsive syn diaxial interactions, a torque is applied around the C(exo)–C(ring)–C(ring)–C(exo) dihedral resulting in the flattening of the ring (Bu–C–C–Bu = 131°). A similar flattening is calculated for BTMSC; however, the energy gained by enhancing attractive Me_3Si interactions in the diaxial conformation is not as great as the decrease in *tert*-butyl/*tert*-butyl repulsions, and this results in a lower relative energy for the twist form in the hydrocarbon.

NMR Structural Assignments. 1,2-Bis(trimethylsilyl)cyclohexane (BTMSC), as well as the 1,3- and 1,4-isomers, was prepared by Eaborn et al.[11] by Li/$EtNH_2$ reduction of the appropriate disilylbenzene, and the cis and trans isomers of BTMSC were separated by preparative GC. One of the two isomers showed a temperature-dependent proton NMR spectrum and was assigned the cis structure. The other isomer did not show a temperature dependant spectrum between room temperature and −80 °C and was assigned the trans structure, which was assumed to be diequatorial. BTMSC was also prepared by Wickham and Kitching[4] by hydrogenation (Rh/C) of 3,4-bis(trimethylsilyl)cyclohexene (BTMSCE) and obtained as a single isomer. An elaborate ^1H and ^{13}C chemical shift argument was presented to justify assignment of the cis structure; however, no temperature-dependent data were reported.

We have repeated the preparation of the mixture of isomers by dissolving metal reduction and were able to duplicate Eaborn's GC separation. We have performed elaborate high-field (400 MHz), NOE, 2D, and dynamic NMR studies of the two isomers. Details of the preparation and the NMR work will be reported elsewhere. We also find one of the isomers (cis) shows a temperature-dependent ^1H NMR spectrum with a coalescence temperature of −50 °C at 200 MHz. On the other hand, the proton spectrum of the trans isomer shows virtually no change between room temperature and −60 °C, indicating essentially one relatively rigid conformer. Several lines of evidence from chemical shifts and NOE convince us that the trans isomer exists as the diaxial conformer. The γ axial hydrogens on C4 and C5 are upfield from all the other ring protons except those on C1 and C2. Those hydrogens show a major NOE with the Me_3Si protons. If the Me_3Si groups were equatorial, no such upfield shift or NOE would be expected. Thus, the available structural evidence strongly supports the calculational results with respect to the preferred conformation.

BTMSCE. Kitching made structural assignments for BTMSC that were derived in part from a prior NMR assignment made for BTMSCE. The assumption was then made that hydrogenation of *cis*-BTMSCE would lead exclusively to *cis*-BTMSC. Consequently, we considered it important to obtain structural information about

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[10] For the sake of consistency with the updated versions of MM2, MM2-82, and MM2-85, we have rerun all the calculations reported in ref 9. While some quantitative differences are found between the results reported herein and ref 9, the qualitative trends, and hence the chemical intuition, are the same. It will also be clear from the previous work that the overall results from the MM2-77 calculations are reasonable and probably acceptable for a qualitative analysis of alkylsilanes.

[11] Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Chem. Soc., Perkin Trans. 1*, **1975**, *1*, 475–477.

Table II. Gauche Interactions in Various Conformations of 1,2-Disilylcyclohexane (DSC) and 1,2-Dimethylcyclohexane (DMC)

	gauche interactions					
	no. × energy					
isomer	SiCCSi	CCCSi	CCCC	total	Δ*H*	MM2 calcd Δ*H*
1,2-DSC						
cis (e,a)	1 × 1.2	2 × 0.5	0	2.2	1.0	0.78
trans (e,e)	1 × 1.2	0	0	1.2	0.0	0.0
trans (a,a)	0	4 × 0.5	0	2.0	0.8	0.69
1,2-DMC						
cis (e,a)	0	0	3 × 0.9	2.7	1.8	1.62
trans (e,e)	0	0	1 × 0.9	0.9	0.0	0.0
trans (a,a)	0	0	4 × 0.9	3.6	2.7	2.44

Table III. Relative Energies of Propylsilane Conformers from MM2 and ab Initio Calculations

conformer	exp	MM2	3-21G(*)// MM2[a]	3-21G(*)// 3-21G(*)[a]	MP3/ 3-21G(*)// 3-21G(*)[a]
180°	0.0	0.0	0.0	0.0	0.0
120°		3.31	3.13	3.05	3.07
gauche	0.6–0.65	0.50	1.08	0.99	0.71
0°		4.68	5.35	5.06	4.71

[a] Notation according to Pople: 3-21G(*)//3-21G(*) implies geometry optimization at the 3-21G(*) level.

BTMSCE from MM2 calculations. The steric energies for the cis and two different trans isomers are shown in Table I. Again, the trans diaxial conformer is more stable than trans diequatorial (0.0 kcal/mol vs 2.2 kcal/mol). The slightly greater stability of the trans diaxial form appears to be due to the removal of the pair of syn diaxial hydrogens at the 1- and 2-positions in the olefin. The major difference between the BTMSC and BTMSCE systems is the rather high relative energy for the cis isomer in BTMSCE. Careful examination of the structures of the BTMSCE minimum energy conformations reveals that the trans diaxial and the cis forms remain flattened half-chairs. On the other hand the trans diequatorial conformer minimizes to a distorted boat form with an Si—C—C—Si angle of 112° and a C=C—C—Si angle of 100.3°, which is close to the energy minimum in allylsilane itself (-103°). We have previously reported the development of torsional parameters for allylic silanes, and these parameters at least partially incorporate stabilizing π interactions between C=C and C—Si bonds that have a mutually perpendicular orientation. Thus it appears that the trans diequatorial form has some means of reducing the steric repulsions that the bulky $SiMe_3$ groups experience (and propagate) while the cis form has no alternative but to exist (as we have found) in the 3-ax, 4-eq conformation. This conformation also results from energy minimization of the 3-eq, 4-ax cis form and is unable to reduce the repulsive interactions (nonbonded and torsional) via a ring-flip or ring pseudorotation. Thus the relative energy of the cis form of the cyclohexenyl system is somewhat larger than for the corresponding hydrocarbon.

DSC and DMC. After completing our calculational studies of BTMSC and DTBC, we chose to examine 1,2-disilylcyclohexane (DSC) and 1,2-dimethylcyclohexane (DMC) systems to determine whether our previous findings of conformer ordering were unique to the aforementioned systems. MM2 calculations were performed on the DMC and DSC systems with use of the parameter set described earlier.[7,9] In DSC one sees the diequatorial conformer being more stable than the diaxial conformer by 0.69 kcal/mol (Table I). The energies of the cis and twist conformers are 0.78 and 5.80 kcal/mol, respectively, relative to the diequatorial conformer.

In 1,2-dimethylcyclohexane (DMC) one sees a slightly different ordering of the relative energies. Here the lowest energy conformation is again the diequatorial, but the energies of the cis form (1.61 relative to trans diequatorial) and the trans diaxial form (2.43 relative to trans diequatorial) are substantially raised compared to DSC (Table I). The differences in relative energies between the various conformers of 1,2-disilylcyclohexane and 1,2-dimethylcyclohexane are probably due to the number and nature of the gauche "butane" interactions. Table II summarizes for chair conformations of DSC and DMC the number of gauche interactions in each. The calculated gauche interaction energy is 1.2 kcal/mol per Si–C–C–Si gauche interaction,[7] 0.5 kcal/mol per gauche C–C–C–Si interaction energy,[1d] and 0.9 kcal/mol per C–C–C–C gauche interaction.[6,12] The values of 1.2 kcal/mol for 1,2-disilylethane and 0.5 kcal/mol for propylsilane are the calculated gauche–anti energy differences. From the above relative energies, the calculated energies of the various conformers of DSC and DMC follow relatively clearly.

Ab Initio Calculations on Model Systems. We have previously reported ab initio calculations on 1,2-disilylethane,[7] which were prompted by the studies reported herein. At that time we did not feel it was imperative to explore the conformational preferences of propylsilane at the ab initio level since the rotational potential we reported[7] seemed to be in reasonable agreement with the available experimental data. However, subsequent investigation by ourselves and Allinger[13] led us to reevaluate the C–C–C–Si potential because of its influence on the relative energies in many of the systems we have discussed herein.

First, we examined the gauche/trans energy difference in propylsilane after including the new bending term for $C–CH_2–Si$.[14] The energy difference was 0.42 kcal/mol, which we felt was low relative to the 0.6–0.65 kcal/mol value reported by Murata, et al.[15a] It appeared that either a small V_1 or V_2 term might be necessary to raise the g–t energy difference to at least 0.50 kcal/mol. Again, we turned to ab initio[15b] calculations on propylsilane to explore the rotational potential function. The results of these investigations are summarized in Table III and as follows:

1. At the MP3/3-21G(*)//3-21G(*) level, the relative energy between the gauche and trans conformations, 0.71 kcal/mol, is in excellent agreement with experiment.

2. The relative energy (g–t) derived from 3-21G(*)//3-21G(*) calculations, 0.99 kcal/mol, is higher than those observed experimentally. We estimate the error in the relative energy at 0.35 kcal/gauche interaction at the 3-21G(*) level.

3. The height of the gauche/gauche barrier with CH_3/SiH_3 eclipsed ranges from 4.71 kcal/mol at MP3/3-21G(*)//3-21G(*) to 5.35 kcal/mol at 3-21G(*)//MM2. Our experience leads us to believe that the actual barrier is closer to 4.3–4.5 kcal/mol and is thus very similar to that found by Durig[16] for butane (see ref 7 and 12). Our current MM2 value, 4.68 kcal, is slightly lower than that reported

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(12) Allinger, N. L.; Profeta, S., Jr. *J. Comput. Chem.* **1980**, *1*, 181.

(13) Allinger, N. L., personal communication.

(14) See footnote 28 in ref 7a. In the MM2-82 and 85 parameter lists distributed by Professor Allinger, a value of 112.7° (θ_0) for $C–CH_2–Si$ is listed, and an examination of the structural data for open chain silanes suggests this value is proper. We have adopted this value in the current studies.

(15) (a) Murata, H.; Matsumara, H.; Ohno, K.; Sato, T. *J. Mol. Struct.* **1979**, *52*. (b) Ab initio calculations were performed by using Gaussian 80 (UCSF).[28] Calculated geometries may be obtained from S.P. by sending a reprint request card.

(16) Durig, J. R.; Compton, D. A. C. *J. Phys. Chem.* **1979**, *83*, 265-268.

previously,[7,9] 4.91 kcal, and more consistent with our expectations.

4. The 3-21G(*) calculated value for the C–C–Si angle, 114.0°, is close to the experimental value[17] for *trans*-propylsilane, 113.2°, and that from MM2, 114.1°.

5. The 3-21G(*) calculated value for the gauche C–C–C–Si angle, 61.3°, is in reasonable agreement with that from MM2, 65.7°.

Having fixed the V_2 term in the C–C–C–Si fragment[18] to yield a larger gauche–trans energy difference (see Table III), and utilizing the larger zero-energy value for the $C-CH_2-Si$ angle, we felt confident that the results of our calculations on systems for which we had experimental data, such as 1-methylsilacyclohexane (MSC) and trimethylsilylcyclohexane (TMSC), would be consistent with the experimental observations and perhaps more reliable than those of Frierson.[1]

Frierson has presented a detailed discussion of the conformational preferences of the MSC and TMSC systems, which we will not repeat here. The previously calculated *A* values were −0.13 kcal and 2.44 kcal/mol respectively. We now calculate −0.19 kcal and 2.75 kcal/mol, which are in good agreement with the experimental estimates of −0.34 kcal[19] and 2.4–2.6 ± 0.1 kcal/mol.[3] We believe that without additional experimental data, further adjustment of the propylsilane torsion function within MM2 is not prudent at this time and are satisfied that the MM2 torsional potential for the C–C–C–Si fragment agrees well with that from the MP3/3-21G(*)//3-21G(*) calculations and with the experimental g–t enthalpy difference.[20]

In addition to propylsilane, we have computed the relative energies for silylcyclohexane, 1,2-disilylcyclohexane, methylcyclohexane, and 1,2-dimethylcyclohexane at the 3-21G(*) and 3-21G levels. These calculations were useful for comparison purposes and to provide essentially "upper limits" of the relative energies. It has been our experience that at the 3-21G and 3-21G(*) levels, the calculated relative energies and barrier heights are systematically overestimated. This trend is somewhat nonlinear, with the relative energies of minima in fully saturated hydrocarbons[12] being the least problematic while substantial errors are found in studies on systems with heteroatoms. Similar conclusions have been reached by Schäfer and his co-workers[21] and Wiberg.[22] We agree with Schäfer's analysis that the 4- or 3-21G bases yield geometries that are quite similar to those from experiment, although the relative energies are not nearly as well reproduced or predicted.[21,23]

Table IV. Comparison of Relative Energies (kcal/mol) from MM2 and ab Initio Calculations of 1-Mono- or 1,2-Disubstituted Cyclohexanes[a]

substituents	conformation	MM2	ab initio[a]
CH_3, H		1.78	2.06
CH_3, CH_3	e,e	0.0	0.0
	e,a	1.62	1.96
	a,a	2.44	2.76
	tw	6.40	8.15

SiH_3, H		1.08	1.98 (3-21G(*)//MM2)
			1.57
			1.18 (MP2/3-21G(*)//3-21G(*))
			1.13 (MP3/3-21G(*)//3-21G(*))

SiH_3, SiH_3	e,e	0.0	0.0
	e,a	0.78	1.16 (3-21G(*)//MM2) 1.24
	a,a	0.69	1.69 (3-21G(*)//MM2) 1.44
	tw	5.80	6.50 (3-21G(*)//MM2)

[a] Hydrocarbon values are for 3-21G//MM2; silanes are for 3-21G(*)//3-21G(*) unless otherwise noted.

In Table IV we list the additional ab initio calculations that were useful in calibrating the additional MM2 parameters needed for our studies of silanes. For the hydrocarbon systems we used single-point 3-21G calculations on MM2 geometries, as we have found these to be generally quite good.[12,24] For methylcyclohexane, the relative energy (ax–eq) is 2.06 kcal/mol, which is in reasonable agreement with the accepted experimental values 1.7–1.8 kcal/mol[25] and previous 4-21G calculations, which yield 1.8–1.98 kcal/mol,[26] and substantially lower than that reported by Pople, et al.,[27] 3.37 kcal/mol, at the STO-3G level with partial optimization. Studies were then performed on MM2 geometries at the 3-21G level for 1,2-dimethylcyclohexane conformations, and we find relative energies (kcal/mol): 0.0 eq/eq, 1.96 eq/ax, 2.76 ax/ax, 8.15 twist; MM2 values are 0.0, 1.62, 2.44, 6.40, respectively. We conclude from these and previous[12] results that the gauche butane interaction is about 0.15 kcal/mol too large from the 3-21G calculations. We wished to establish the magnitude of this value in the 1,2-disubstituted hydrocarbon to serve as a reference point for discussion of our results on the mono- and disilylcyclohexane models.

Our model studies proceeded next to silylcyclohexane, for which we could not find any data on the *A* value of the SiH_3 group. Using the MM2-82 parameter set and our new torsion terms, we find an *A* value of 1.08 kcal/mol. The value from full cartesian geometry optimizations using GAUSSIAN 80-UCSF[28] is 1.57 kcal/mol, which is about 80% of the total gauche propylsilane energy at the 3-21G(*) level (0.80 × 0.99 × 2 interactions). It is worthwhile to note that the energy difference derived from 3-21G(*)//MM2 calculations was 1.98 kcal/mol, a value substantially in excess of what we believe to be reasonable. However this value reflects the overestimation of the trans conformation stability as seen in propylsilane at the 3-21G(*)//3-21G(*) and 3-21G(*)//MM2 levels. The reason for this problem probably lies with the modest representation of the basis set used, and with the lack of correlation energy, as the MM2 structures are in very good agreement with those from the 3-21G(*) optimizations, save the systematic shortening of the C–H bonds from the ab initio calculations. Furthermore, post Hartree–Fock Møller–Plesset calculations, which include treatment of correlation effects (MP2 and MP3/3-21G(*)//3-21G(*)), corroborate our suggestion that the relative energy of the SiH_3 group in the axial position is closer to 1.1–1.2

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[17] Hayashi, M.; Nakagawa, J.; Aguni, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2468.

[18] The new C–C–C–Si torsion term: $V_1 = 0.0$, $V_2 = 0.10$, $V_3 = 0.50$; θ_0 for $C-CH_2-Si = 112.7$ ($K_b = 0.40$).

[19] Carleer, R.; Anteunis, M. J. O. *Org. Magn. Reson.* **1974**, *12*, 673.

[20] However, we are concerned about the inability of MM2 to reproduce the half-chair/envelope energy difference in silacyclopentane (exp. 3.89; Frierson 3.23; current work 3.14 kcal/mol). We agree with Professor Allinger, however, that there may be a possible error in the experimental value.

[21] Schäfer, L.; Ewbank, J. D.; Klimkowski, V. J.; Siam, K. *J. Mol. Struct.* (*THEOCHEM*) **1986**, *135*, 141–158 and references therein.

[22] Wiberg, K. B.; Martin, E. *J. Am. Chem. Soc.* **1985**, *107*, 5035–5041. Wiberg, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 5817–5822.

[23] Shäfer, L., personal communication.

[24] Profeta, S., Jr.; Allinger, N. L., unpublished observations.

[25] Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. *Conformational Analysis*; Wiley Interscience: New York, 1965.

[26] Klimkowski, V. J.; Manning, J. P.; Schäfer, L. J. *J. Comput. Chem.* **1985**, *6*, 570–580.

[27] Cremer, D.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 6836–6839.

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kcal/mol. While we have not yet performed these correlation energy calculations at the 6-31G(*)//6-31G(*) level, we anticipate doing so and finding that there is a reasonable quantitative agreement with the results reported herein.

The next systems studied were the 1,2-disilylcyclohexanes. Again, full cartesian geometry optimizations completed at the 3-21G(*) level gave the results listed in Table IV. The 3-21G(*) structures are in excellent agreement with those from MM2. The 3-21G(*)//MM2 results for these systems are also reported. The relative energies from these latter calculations were, we felt, systematically too large, particularly when compared to the MM2 values. Thus, the optimizations were performed to see if the energy differences would approach those from MM2. Clearly, there remain substantial differences between the ab initio calculations and MM2; however, we feel that we have accounted for the bulk of the discrepancies in our analysis of propylsilane and silylcyclohexane. Indeed, if the relative energies from the ab initio calculations at the 3-21G(*) level were in better agreement with the MM2 calculations, that would need to be interpreted as *very* serendipitous. The relative energies from the 3-21G(*) optimizations, while systematically larger than those we find from MM2, reflect the diminished steric repulsions and perhaps even some of the attractive nonbonded interactions present in these systems when compared to their hydrocarbon analogues. It is possible that we will find better agreement between the ab initio and MM2 results for the ordering of relative energies in these systems when we reexamine them at the 6-31G(*)//6-31G(*) level and include electron correlation (MP2/MP3). Our conclusions concerning the unusual conformational energetics of the BTMSC isomers appear to be consistent with the overall trends in the conformational behavior of the 1,2-disubstituted cyclohexanes as far as we are currently able to characterize it.

Complete structural details will not be published here; this data can be obtained from one of us (S.P.) by submitting a reprint request for the same.

Conclusions

We may summarize our findings as follows:

1. In the model system, propylsilane, a gauche energy of 0.5–0.6 kcal/mol is found by experiment and MM2. Ab initio calculations at the 3-21G(*) level overestimate this relative energy by 0.35 kcal/mol.
2. The calculated structures of propylsilane are in good agreement with experiment.
3. Relative energies in methylcyclohexanes are seen as approximately linearly additive based on a gauche butane energy of 0.9 kcal/mol. The energies from 3-21G//MM2 calculations appear to overestimate this energy by 0.1–0.15 kcal/mol.
4. The relative energies of silyl- and 1,2-disilylcyclohexanes from 3-21G(*) optimizations also reflect the error in the gauche propylsilane energy in an additive fashion. However, the relative energy trends, that is, the higher energy silane conformers are stabilized relative to the hydrocarbons, are clearly shown.
5. In 1,2-bis(trimethylsilyl)cyclohexanes, attractive nonbonded interactions dominate the conformational features of these isomers, and this results in the unusual stability of the trans diaxial conformer. In 1,2-di-*tert*-butylcyclohexanes, nonbonded repulsions dominate, and the trans diaxial and twist-boat forms maximize relief of these repulsions.

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Appendix. A listing of the torsion, stretching, dipole, van der Waals, and stretch–bend parameters used in this work appears in the Appendix.

Registry No. *cis*-BTMC, 55860-94-1; *trans*-BTMC, 55860-93-0; *cis*-BTBC, 20065-94-5; *trans*-BTBC, 20065-95-6; DSC, 116910-62-4; *cis*-DSC, 116910-59-9; *trans*-DSC, 116910-60-2; DMC, 583-57-3; *cis*-DMC, 2207-01-4; *trans*-DMC, 6876-23-9; *cis*-BTMSCE, 84280-55-7; *trans*-BTMSCE, 116910-61-3; propylsilane, 13154-66-0; silylcyclohexane, 18162-96-4; methylcyclohexane, 108-87-2.

Supplementary Material Available: Tables of MM2-calculated steric energy components for conformers of BTMSC, DTBC, BTMSCE, DSC, and DMC, calculated torsional angles for BTMSC and DTBC, and figures showing the calculated structures for conformers of BTMSC and DTBC (9 pages). Ordering information is given on any current masthead page.

Appendix. MM2 Parameters Used in Current Studies[a]

							comments or ref
				I. Torsion Parameters			
30	30	19	5	0.0	0.0	0.272	ref 1
1	30	19	5	0.0	0.0	0.272	ref 1
5	30	19	5	0.0	0.0	0.176	ref 1
1	1	30	30	0.200	0.270	0.093	
5	1	30	30	0.0	0.0	0.267	
1	19	30	30	0.0	0.0	0.167	ref 1
30	19	30	30	0.0	0.0	0.167	ref 1
30	30	19	30	0.0	0.0	0.167	ref 1
1	30	1	1	0.200	0.270	0.093	
1	1	1	30	0.200	0.270	0.093	
30	1	1	30	0.200	0.270	0.093	
5	1	1	30	0.0	0.0	0.267	
1	1	30	5	0.0	0.0	0.267	
1	30	1	5	0.0	0.0	0.267	
5	1	19	30	0.0	0.0	0.200	ref 1
1	19	30	1	0.0	0.0	0.167	correct value from
30	19	30	1	0.0	0.0	0.167	Frierson's dissertation
1	30	19	30	0.0	0.0	0.167	Frierson's dissertation
1	30	30	19	0.0	0.101	0.500	new $V_2 = 0.101$
1	1	30	19	0.0	0.101	0.500	new $V_2 = 0.101$
1	1	30	19	0.0	0.101	0.500	new $V_2 = 0.101$
5	1	30	19	0.0	0.0	0.105	ref 1
5	30	30	19	0.0	0.0	0.105	ref 1

Appendix (Continued)

							comments or ref
1	19	30	5	0.0	0.0	0.200	ref 1
30	19	30	5	0.0	0.0	0.200	ref 1
5	1	30	5	0.0	0.0	0.237	
19	30	30	19	0.00	0.710	0.000	ref 7
1	30	30	1	0.20	0.270	0.093	
1	30	30	5	0.0	0.0	0.267	
5	30	30	5	0.00	0.0	0.237	
				II. Stretching Parameters			
5	30	4.6		1.113			ref 6
30	30	4.4		1.563			
1	30	4.4		1.538			
19	30	2.97		1.880			ref 1
				III. Dipole Parameters			
19	30	0.600					ref 1
				IV. van der Waals Parameters			
	30	0.044		1.900			ref 6
				V. Bending Parameters			
1	1	30		0.450	109.47		all from ref 1 and 6
1	30	1		0.450	109.47		unless otherwise noted
1	30	30		0.450	109.47		
5	1	30		0.360	109.39	1	
5	1	30		0.360	109.39	2	
5	1	30		0.360	110.00	3	
5	30	30		0.360	109.39	1	
5	30	30		0.360	109.39	2	
5	30	30		0.360	110.00	3	
1	30	5		0.360	109.39	1	
1	30	5		0.360	109.39	2	
1	30	5		0.360	110.00	3	
5	30	5		0.320	109.40	1	
5	30	5		0.320	109.00	2	
5	30	5		0.320	109.47	3	
1	19	30		0.480	110.80	1	
1	19	30		0.480	110.40	2	
1	19	30		0.480	108.50	3	
30	19	30		0.480	110.80	1	
30	19	30		0.480	110.40	2	
30	19	30		0.480	108.50	3	
5	19	30		0.460	109.30	1	
5	19	30		0.460	107.00	2	
5	19	30		0.460	110.20	3	
1	30	19		0.400	109.00	1	
1	30	19		0.400	110.90	2	
1	30	19		0.400	112.70	3	
19	30	1		0.400	109.00	1	
19	30	1		0.400	110.90	2	
19	30	30		0.400	109.00	1	
19	30	30		0.400	110.90	2	
19	30	30		0.400	112.70	3	
19	30	5		0.320	108.60	1	from MM2-85 parm listing
19	30	5		0.320	110.80	2	
19	30	5		0.320	107.00	3	
5	30	19		0.320	108.60	1	from MM2-85 parm listing
5	30	19		0.320	110.80	2	
5	30	19		0.320	107.00	3	
1	30	19		0.400	109.00	1	
1	30	19		0.400	110.90	2	
1	30	19		0.400	112.70	3	from MM2-85 parm listing
5	19	5		0.38	104.50	1	
5	19	5		0.38	108.70	2	
5	19	5		0.38	109.50	3	
				VI. Stretch–Bend Parameters			
0.12		0.200		0.09	0.06		ref. 1

[a] We have used the above parameters in the standard QCPE release of MM2-77 and in the VAX/VMS version developed by one of us (S.P.), which is also MM2-77. Neither of these programs include the "polarization" correction to bond lengths as has been incorporated into the 1982 and 1985 releases of MM2. To compensate for this we have assigned the atom type of 30 to carbon atoms which occur in an Si–C–C–Si fragment. This promotes a substantial proliferation of parameters, as can be seen above; however, these can be readily incorporated into any standard MM2 data file and used ad infinitum. The additional parameters supplied in the list above, which are pertinent atom type 30, are unnecessary in the MM2-82 and 85 programs. However, any new parameters developed can be used in any version of the MM2 program.