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sp^2-Hybridized Silicon: Parameters for Molecular Modeling

A.G. Brook*

Lash Miller Chemical Laboratories, University of Toronto, Toronto, M5S 1A1, Canada

J.J. Gajewski

Department of Chemistry, Indiana University, Bloomington, Indiana, 47401 U.S.A

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ABSTRACT

A set of mutually compatible torsional, stretch, and bending parameters have been devised that reproduce with considerable accuracy the calculated structures of simple silenes and disilenes, and the crystal structure data available for solid silenes and disilenes.

The current interest in modeling all types of molecules, using readily available modeling programs, has made desirable the availability of parameters for an increasing number of atom types. We have addressed the problem of sp^2-hybridized silicon, in view of the interest of one of us in silenes and their behavior. The availability of good quality ab initio or other calculations on simple silenes and disilenes, and the availability of crystal structure data for a few solid silenes and disilenes, provide data that can be used in developing the required parameters.

The parameter lists given below meet the object of duplicating simultaneously the structures of simple silenes, such as silene [1], dimethylsilene [1], and bis(silyl)silene [1], as well as the reported crystal structures of $(Me_3Si)_2Si{=}CAd(OSiMe_3)$ [2] (Ad = 1-adamantyl) and $Me_2Si{=}C(SiMe_3)SiMe(Bu\text{-}t)_2$ [3], and in addition disilenes such as disilene [4], tetramethyldisilene [4], and the crystalline disilenes tetramesityldisilene [5], *trans*-1,2-dimesityl-1,2-di(*t*-butyl)disilene [5], and tetra(2,6-diethylphenyl)disilene [6].

The modeling program employed was PF, an IBMPC program that is an experimental enhanced version of PCMODEL [7] at the beta testing stage. Since the force field employed, MMX, is essentially the same as MM2 [7] and mainly employs the MM2 parameters for carbon, hydrogen, silicon, and other common atoms, the parameters developed from this research are applicable to any modeling program that uses the MM2 force field.

Most of the parameters required were common to both the silenes and disilenes and are in the top part of Table 1. To this main group some additional torsional parameters had to be added, depending on whether silenes that contained a trimethylsiloxy group (Me_3SiO) attached to sp^2-hybridized carbon or disilenes were to be modeled. This use of two data bases was necessary because the modeling program employed allowed only a maximum of 50 torsional values to be entered in an added constants data set, but two would not be necessary in a modeling program not having this restriction.

The program, as utilized, allows the differentiation between simple sp^2-hybridized carbon atoms (as in C=C or Si=C) and an aromatic-type carbon atom (as in a phenyl group) in response to an added constants file with a name beginning with ARET (see below). This was necessary in order to obtain satisfactory bond lengths for aromatic silenes (Ar—Si=C) or disilenes (Ar—Si=Si), where the length of an Ar—Si bond is distinctly different from that of the Si=C bond (1.90 and 1.70 Å), there being little evidence of conjugation between an aromatic ring and an sp^2-hybridized silicon atom. (This problem is normally handled in another way by this program when aryl-substituted alkenes are involved). Thus it was necessary to provide parameters in Table 1, such as torsion values for atom

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[*] To whom correspondence should be addressed.

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TABLE 1 Force Field Parameters for Silenes and Disilenes[a]

Atom[b]	*van der Waals radius*	*Hardness*	*Bond*	*Bond dipole, μ*
Si$_{sp^2}$	2.300	0.147	Si$_{sp^2}$=C$_{sp^2}$	0.84
			Si$_{sp^2}$=Si$_{sp^2}$	0.00
			C—Si$_{sp^2}$	−0.70
			H—Si$_{sp^2}$	0.00
			Si—Si$_{sp^2}$	0.30
			C$_{ar}$—Si$_{sp^2}$	−0.70
			H—C$_{ar}$	0.20
			C—C$_{ar}$	0.30

Bond	L_o	*Stretching* K_s *(MMX)*[c]
Si$_{sp^2}$=C$_{sp^2}$	1.701	5.000
Si$_{sp^2}$—C	1.890	4.500
Si$_{sp^2}$—H	1.475	4.600
Si$_{sp^2}$—Si	2.330	3.500
Si$_{sp^2}$=Si$_{sp^2}$	2.140	3.000
C$_{ar}$—Si$_{sp^2}$	1.880	4.500
C$_{ar}$—H	1.101	4.600
C$_{ar}$—C	1.497	5.000

Angle	θ	*Bending* K_θ *(MMX)*	*Angle*	θ	K_θ *(MMX)*
C$_{sp^2}$–Si$_{sp^2}$–C$_{sp^2}$	120.00	0.301	C$_{sp^2}$–Si$_{sp^2}$–C$_{ar}$	120.00	0.301
C–Si$_{sp^2}$–C$_{sp^2}$	123.00	0.500	C–Si$_{sp^2}$–C	113.50	0.400
C–C$_{sp^2}$–Si$_{sp^2}$	126.00	0.400	H–C$_{sp^2}$–Si$_{sp^2}$	124.80	0.550
H–C–Si$_{sp^2}$	109.39	0.360	Si–C$_{sp^2}$–Si$_{sp^2}$	123.00	0.400
Si–C$_{sp^2}$–Si	120.00	0.400	C–Si–Si$_{sp^2}$	110.20	0.400
C$_{sp^2}$–Si$_{sp^2}$–Si	119.00	0.200	O–C$_{sp^2}$–Si$_{sp^2}$	120.50	0.700
C$_{sp^2}$–O–Si	127.40	0.200	Si–Si$_{sp^2}$–Si	122.00	0.800
C–Si–O	108.50	0.350	Si–O–1*p*	97.50	0.350
H–Si–Si$_{sp^2}$	108.50	0.240	C$_{sp^2}$–Si$_{sp^2}$–H	123.20	0.252
H–Si$_{sp^2}$–H	114.00	0.224	C–Si$_{sp^2}$–Si$_{sp^2}$	123.50	0.500
C$_{ar}$–Si$_{sp^2}$–Si$_{sp^2}$	126.00	0.700	H–Si$_{sp^2}$–Si$_{sp^2}$	120.00	0.252
C$_{ar}$–Si$_{sp^2}$–C$_{ar}$	121.00	0.500	C$_{ar}$–C$_{ar}$–Si$_{sp^2}$	122.50	0.430
C–C–Si$_{sp^2}$	109.00	0.450	C–Si$_{sp^2}$–Si	120.00	0.280
C$_{ar}$–C$_{ar}$–C$_{ar}$	120.00	0.430	H–C$_{ar}$–C$_{ar}$	120.00	0.360
C–Si$_{sp^2}$–C$_{ar}$	112.00	0.300	C–C$_{sp^2}$–Si	120.00	0.400
C–C$_{ar}$–C$_{ar}$	121.40	0.550	H–C–C$_{ar}$	109.39	0.360
C–C$_{sp^2}$–O	112.00	0.800	C–C–C$_{ar}$	109.47	0.450

	Torsions for both silenes and disilenes		
Bonds	V_1	V_2	V_3
C—C—Si$_{sp^2}$—C$_{sp^2}$	−0.308	0.168	0.042
C—Si—Si$_{sp^2}$—C	0.000	0.000	0.245
C—C—Si$_{sp^2}$—Si	0.000	0.000	0.245
C—C$_{sp^2}$—Si$_{sp^2}$—C	−0.100	8.000	0.000
H—C$_{sp^2}$—Si$_{sp^2}$—C	0.000	8.000	0.000
H—C—Si$_{sp^2}$—C	0.000	0.000	0.378
H—C—Si$_{sp^2}$—C$_{sp^2}$	0.000	0.000	−0.190
Si—C$_{sp^2}$—Si$_{sp^2}$—C	0.000	8.000	0.000
Si$_{sp^2}$—C$_{sp^2}$—Si—C	0.000	0.000	0.000
Si—C$_{sp^2}$—Si—C	0.000	0.000	0.350
H—C—Si—Si$_{sp^2}$	0.000	0.000	0.117
C—Si—Si$_{sp^2}$—C$_{sp^2}$	−0.310	−0.168	0.042
C—C$_{sp^2}$—Si$_{sp^2}$—Si	0.000	8.000	0.000
C—C—C$_{sp^2}$—Si$_{sp^2}$	−0.440	0.240	0.060
C—Si—Si$_{sp^2}$—Si	−0.310	−0.168	0.042

TABLE 1 (*continued*)

Bonds	*Torsions for both silenes and disilenes*		
	V_1	V_2	V_3
H—C$_{sp^2}$—Si$_{sp^2}$—Si	0.000	8.000	0.000
H—Si—Si$_{sp^2}$—Si	0.000	0.000	0.378
H—Si—Si$_{sp^2}$—C$_{sp^2}$	0.000	0.000	0.000
H—C$_{sp^2}$—Si$_{sp^2}$—H	0.000	8.000	0.000
C$_{ar}$—C$_{ar}$—C$_{ar}$—Si$_{sp^2}$	−0.930	15.000	0.000
C—C$_{ar}$—C$_{ar}$—Si$_{sp^2}$	−0.270	15.000	0.000
C$_{ar}$—C$_{ar}$—Si$_{sp^2}$—C$_{ar}$	0.100	0.000	0.500
H—C$_{ar}$—C$_{ar}$—Si$_{sp^2}$	0.000	15.000	0.000
H—C—C—Si$_{sp^2}$	0.000	0.000	0.105
C$_{ar}$—C$_{ar}$—Si$_{sp^2}$—C	−0.440	−0.240	0.060
C—C—Si$_{sp^2}$—C$_{ar}$	0.280	0.021	0.350
H—C—C$_{sp^2}$—Si$_{sp^2}$	0.000	0.000	−0.240
C—C$_{sp^2}$—Si$_{sp^2}$—C$_{ar}$	−0.100	8.000	0.000
H—C$_{sp^2}$—Si$_{sp^2}$—C$_{ar}$	0.000	8.000	0.000
C$_{ar}$—C$_{ar}$—Si$_{sp^2}$—C$_{sp^2}$	0.100	0.000	0.500
C$_{ar}$—C$_{ar}$—C$_{ar}$—C$_{ar}$	0.000	15.000	1.000
H—C$_{ar}$—C$_{ar}$—C$_{ar}$	0.000	15.000	0.000
H—C$_{ar}$—C$_{ar}$—H	0.000	15.000	0.000
H—C—Si$_{sp^2}$—C$_{ar}$	0.000	0.000	0.117
C—C$_{sp^2}$—Si—C	0.000	0.000	0.350
Si—C$_{sp^2}$—Si$_{sp^2}$—C$_{ar}$	−0.100	8.000	0.000
H—C—C$_{sp^2}$—Si	0.000	0.000	0.350
C—C$_{ar}$—C$_{ar}$—C$_{ar}$	−0.270	15.000	0.000
H—C—C$_{ar}$—C$_{ar}$	0.000	0.000	−0.240
C—C$_{ar}$—C$_{ar}$—H	0.000	15.000	0.000
C—C—C$_{ar}$—C$_{ar}$	−0.440	0.240	0.060
H—C—Si$_{sp^2}$—Si	0.000	0.000	0.378
Additional torsions to be added to above data for silenes with Me$_3$SiO on C$_{sp^2}$			
Si$_{sp^2}$—C$_{sp^2}$—O—Si	2.350	1.550	−2.350
O—C$_{sp^2}$—Si$_{sp^2}$—C	−1.200	8.000	0.000
O—C$_{sp^2}$—Si$_{sp^2}$—Si	−1.200	8.000	0.000
Si$_{sp^2}$—C$_{sp^2}$—O—1p	0.000	0.000	0.000
C$_{sp^2}$—O—Si—C	0.000	0.000	0.230
C—C$_{sp^2}$—O—Si	2.350	1.550	−2.350
1p—O—Si—C	0.000	0.000	0.000
H—C—Si—O	0.000	0.000	0.210
Additional torsions to be added to main torsions above for disilenes			
C—Si$_{sp^2}$—Si$_{sp^2}$—C	−0.100	5.000	0.000
C—Si$_{sp^2}$—Si$_{sp^2}$—C$_{ar}$	−0.270	5.000	0.000
C$_{ar}$—Si$_{sp^2}$—Si$_{sp^2}$—C$_{ar}$	−0.270	5.000	0.000
C—C—Si$_{sp^2}$—Si$_{sp^2}$	−0.310	0.168	0.042
C$_{ar}$—C$_{ar}$—Si$_{sp^2}$—Si$_{sp^2}$	0.100	0.500	0.000
H—C—C—C$_{ar}$	0.000	0.000	0.500
H—C—Si$_{sp^2}$—Si$_{sp^2}$	0.000	0.000	−0.168
H—Si$_{sp^2}$—Si$_{sp^2}$—H	0.000	5.000	0.000

1p denotes lone pair of electrons.

[a] Units: distance, Å; dipole moments, D; bending angles, °; stretching constants, mdyne Å^{-1}; bending constants, mdyne rad^{-2}; torsional constants, kcal mol^{-1} deg^{-1}.

[b] Atom types; C, type 1; C$_{sp^2}$, type 2; H, type 5; Si, type 19; 1p, type 20; C$_{ar}$, type 40; Si$_{sp^2}$, type 59.

[c] MMX is the force field used by the programs PF and PCMODEL.

types H–C$_{ar}$—C$_{ar}$—C$_{ar}$, which do not involve silicon at all: their values are identical to the values in the PF data files for simple sp^2-hybridized carbon (e.g., H—C$_{sp^2}$—C$_{sp^2}$—C$_{sp^2}$).

A value for the hardness of sp^2-hybridized silicon (0.147) was taken from the literature [8], and its van der Waals radius (2.300 Å) was estimated [9]. The length of a C$_{sp^3}$ single bond to sp^2-hybridized silicon was taken as 1.89 Å, that of C$_{ar}$—Si$_{sp^2}$ as 1.88 Å, and that of a silicon–carbon double bond as 1.70 Å, which are averages of reported values. The length of a silicon–silicon double bond was taken as 2.14 Å and other bond lengths were chosen after consideration of the results of calculations and crystal structure data. Values for the stretching force constants of the silicon–carbon and silicon–silicon double bond were approximated using Badger's rule [10] and scaled to the value of 9.600 mdyn $Å^{-1}$ used for C═C in the MMX data file of PF. After trial and error calculations, the values of 5.00 and 3.00 mdyn $Å^{-1}$ were employed. The former value is in close agreement with a proposed value of 5.14 [11]. The bond moment for the Si═C bond was taken as 0.84 D [11].

Values for bending and torsion angles and force constants involving silicon were initially obtained by using the corresponding values in the MMX [or MM2(85)-PC [12]] data files for the analogous carbon situation; e.g., the parameters for the atom sequence Si—C═C were employed for the sp^2-hybridized silicon analog Si—Si═C. The value of the bending (or torsion) force constant was then reduced by 30% for all cases in which silicon was the central atom of the triad (or tetrad for torsion parameters), based on evidence that an angle involving silicon is much more easily deformed than one involving a carbon atom.

A minimum set of required parameters to allow modeling of the known simpler silenes and disilenes was then further adjusted by trial and error, by changing both the angles and force constants, until as good a fit as possible was reached for all the compounds tested. Then the more complex structures were introduced, with the addition of further necessary parameters and the further alteration of force constants and angles to obtain as close a fit as possible for all the structures considered.

RESULTS

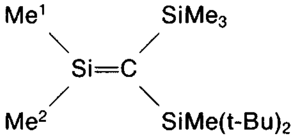
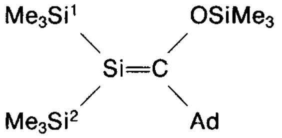
The data for silenes listed in Table 2 demonstrate that the parameter set used reproduces reported bond lengths to within three or four hundreths of an angstrom unit, and bond angles within a few tenths of a degree in most cases, despite the great differences in the structures studied. It is recognized that bond lengths from crystal structures may vary significantly from true values, or from those derived from ab initio calculations: no attempt was made here to correct for the different kinds of data being considered. The crystal structure data for the Wiberg silene $Me_2Si{=}C(SiMe_3)SiMe(Bu\text{-}t)_2$[3] were fairly accurately reproduced, as were the data for the Brook silene $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$[2], although in the latter case one significant problem was encountered. Thus, the angle ═C—O—SiMe$_3$ reported in the crystal structure was remarkably large, 134°, and the angle O–C_{sp^2}—C (of the adamantyl group) was remarkably small (112.2°). It is recognized that some of these angle distortions from the norm may be due to crystal packing forces, as well as to severe steric interactions between bulky groups. Since bending parameters for the C_{sp^2}—O—Si angle do not exist in the MMX data files, a large value for the angle (127.4°) could be introduced in the added data set, which resulted in a good fit. In the case of C_{sp^3}—C_{sp^2}—O (crystal structure value 112.2°), a bond angle (120°) and bending force constant exist in the data base; however, when these values were used the modeling program invariably predicted a bond angle of not less than 116.5°, more than 4° larger than the observed value, regardless of the parameters employed for the other bond angles at the sp^2-hybridized carbon atom [i.e., Si═C—O and Si═C—C(Ad)]. A close fit could be forced by employing an alternative bond angle (112°) and appropriate force constant for C_{sp^3}—C_{sp^2}—O.

With the addition of some further parameters, it was possible to model a number of disilenes successfully, as shown in Table 3. Agreement of bond lengths and bond angles with the calculated results of two simple silenes was excellent, and the agreement of bond lengths with the reported values for three crystalline disilenes was again within a few hundredths of an angstrom. The computed values of bond angles in these highly hindered species did not agree with the observed x-ray structure values as well as was found with the silenes, but the structures resulting from minimization generally reproduced the main features of the crystal structures, and crystal packing forces could easily account for the deviations noted. Major deviations from the crystal structure appeared to be found with tetramesityldisilene, as shown in Table 3, particularly for the angles formed by the planes of the mesityl groups with the disilene framework. However, the data reported in Table 3 are for a 1 : 1 disilene–toluene solvate [15] (where the location of the toluene in the crystal lattice appears to account for the very different orientations of the pairs of mesityl groups relative to the Si═Si bond [16]). Hence comparisons between the crystal structure data for the solvated disilene and the modeled structure are not entirely appropriate.

Some data have now been reported for the nonsolvated disilene [16]. The Si═Si bond length, 2.14 Å, is in closer accord with that of other reported disilenes, and close to that calculated, and the angles (42, 52, 67, and 70°) made by the planes of the mesityl groups with the Si═Si framework, although indicating a surprisingly unsymmetrical structure, have sizes in much closer agreement with the values found from the calculations (55 and 57°) than was found for the toluene-solvated species.

In all of the disilenes, the sp^2-hybridized silicon atoms were found to be essentially planar, and it was not found possible to duplicate the reported pyramidalization [5,16] of the silicon atoms in tetramesityldisilene by variation of the parameters used in the modeling. This unusual effect may be

TABLE 2 PF-Calculated and Reported Structural Features[a] of Silenes

Compound	*Structural feature*	*This work*	*Lit. value*	*Ref*
$H_2Si{=}CH_2$	H—Si	1.47	1.475	[1]
	Si=C	1.70	1.70	
	C—H	1.10	1.10	
	H—Si—H	113.9	113.95	
	H—Si=C	123.05	123.20	
	Si=C—H	122.5	121.39	
	H—C—H	115.1	117.21	
$Me_2Si{=}CH_2$	H—CH_2	1.11	1.09	[1]
	Me—Si	1.89	1.89	
	Si=C	1.70	1.70	
	C—H	1.10	1.09	
	Me—Si—Me	113.6	113.5	
	Me—Si=C	123.2	123.4	
	Si=C—H	122.4	122.6	
	H—C—H	115.1	114.8	
	Me^1—Si	1.89	1.85	[3]
	Me^2—Si	1.89	1.84	
	Si=C	1.72	1.70	
	C—$SiMe_3$	1.88	1.86	
	C—SiMe	1.90	1.89	
	Me^1—Si—Me^2	104.1	104.0	
	Me^1—Si=C	127.1	127.0	
	Me^2—Si=C	128.8	129.0	
	Si=C—$SiMe_3$	118.9	119.5	
	Si=C—SiMe	122.7	122.8	
	Me_3Si—C—SiMe	118.4	117.7	
	Twist[b]	1.4	1.6	
$(H_3Si)_2Si{=}CH_2$	H—Si	1.48	1.485	[1]
	Si—Si	2.34	2.346	
	Si=C	1.70	1.718	
	C—H	1.10	1.082	
	H—Si—Si	109.8	110.4	
	Si—Si—Si	121.8	120.3	
	Si—Si=C	119.1	119.8	
	Si=C—H	122.5	122.8	
	H—C—H	115.0	114.4	
	Me—Si	1.88–1.89	1.88–1.90	[2]
	Si^1—Si	2.34	2.34	
	Si^2—Si	2.34	2.35	
	Si=C	1.72	1.76	
	C—O	1.36	1.40	
	O—$SiMe_3$	1.64	1.66	
	C—Ad	1.53	1.52	
	Si^1—Si=C	116.3	114.6	
	Si^2—Si=C	126.0	126.5	
	Si^1—Si—Si^2	117.6	118.9	
	Si=C—O	118.0	117.4	
	C—O—$SiMe_3$	134.1	134.0	
	Si=C—Ad	129.8	130.1	
	O—C—Ad	112.2	112.2	
	Twist[b]	11.7	14.3	

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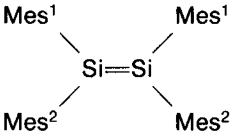
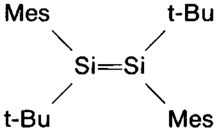
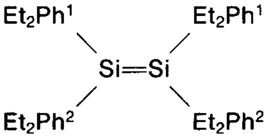
[a] Units: bond lengths, Å; bond angles, °; dihedral angles, °.

[b] Twist, as used here, is the dihedral angle between the vector joining the two atoms directly attached to sp^2-hybridized silicon and the vector between the two atoms directly attached to sp^2-hybridized carbon.

TABLE 3 PF-Calculated and Reported Structural Features[a] of Disilenes

Compound	*Structural feature*[b]	*This work*	*Lit. value*	*Ref*
$H_2Si{=}SiH_2$	H—Si	1.47	1.48	[4]
	Si—Si	2.14	2.156	
	H—Si=Si	121.9	121.9	
	H—Si—H	116.2	116.2	
$Me_2Si{=}SiMe_2$	Me—Si	1.89	1.898	[4]
	Si=Si	2.14	2.133	
	Me—Si=Si	123.4	123.15	
	Me—Si—Me	113.1	113.3	
	Mes^1—Si	1.90	1.871	[5]
	Mes^2—Si	1.90	1.880	
	Si=Si	2.15	2.16 (2.14)	[16]
	Mes^1—Si=Si	123.0	126.7	
	Mes^2—Si=Si	121.6	113.9	
	Mes^1—Si—Mes^2	115.4	115.6	
	Mes^1—Si=Si dihed.	55	35 (42, 52)	[16]
	Mes^2—Si=Si dihed.	57	78 (67, 70)	[16]
	Si=Si twist[c]	4.0	9.4 (3)	[16]
	Mes—Si	1.90	1.884	
	t—Bu—Si	1.91	1.904	
	Si=Si	2.14	2.143	
	Mes—Si=Si	123.2	123.86	
	t—Bu—Si=Si	122.6	122.77	
	Mes—Si—t—Bu	114.2	113.2	
	Mes—Si=Si dihed.	89	88	
	Si=Si twist[c]	0.25	0.07	
	Et_2Ph^1—Si	1.90	1.886	[6]
	Et_2Ph^2—Si	1.90	1.878	
	Si=Si	2.16	2.140	
	Et_2Ph^1—Si=Si	120.6	117.6	
	Et_2Ph^2—Si=Si	121.8	124.8	
	Et_2Ph^1—Si—Et_2Ph^2	117.6	117.6	
	Et_2Ph^1—Si=Si dihed.	58	62	
	Et_2Ph^2—Si=Si dihed.	57	64	
	Si=Si twist[c]	9.1	10	

[a] Units: bond lengths, Å; bond angles, °; dihedral (dihed.) angles, °.

[b] Et_2Ph = 2,6-diethylphenyl.

[c] Twist, as used here, is measured by the dihedral angle between the vectors joining the ring carbon atoms of the aryl groups attached to silicon atom 1 and the ring carbon atoms of the aryl groups attached to silicon atom 2 of the disilene.

due to crystal packing forces, as was suggested by West and coauthors [5].

Only very limited testing of the reliability of these parameter sets for predicting results was possible. It is known [17] that photolysis of $(Me_3Si)_2(t\text{-}Bu)SiCOAd$ yields only one of the two possible geometric isomers of the silene $Me_3Si(t\text{-}Bu)Si{=}C(OSiMe_3)Ad$: this species can be observed and characterized by NMR spectroscopy, but its geometry is unknown. Modeling of the two isomers gives relative energy data which indicate that the *E* isomer (Me_3Si and Ad groups on the same side of the double bond) is the stabler of the pair, as would be predicted purely on steric grounds. Several other related systems were similarly tested: in each case the modeling program indicated that the silene predicted to be less strained, based on steric arguments, was the more stable isomer.

It appears that, if appropriate precautions are taken in interpreting the data derived from this set of parameters, reasonable modeling of a wide structural variety of silenes and disilenes can be effected.

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References and Notes

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[7] PCMODEL contains the MMX force field, which for hydrocarbons and silicon systems is identical to MM2 except for larger C_{sp} out-of-plane bending constants (0.6) and lower C_{sp} bending constants (0.15), and a $H–C_{sp^2}$ bond moment of 0.2 D. Both PCMODEL and PF are available from Serena Software, P.O. Box 3076, Bloomington, Indiana, 47402 U.S.A. Since sp^2-hybridized silicon is not one of the standard atom types in any of the common modeling programs, a type-59 atom, symbol Z2, one of the wild-card atoms provided in the MMX force field used in the program PF, was employed. Thus the added constants data set ARET-SIL.STO, containing the parameters listed in the first two sections of Table 1, was used as an added data set for silenes and employed entries such as 59-2 to represent $Si_{sp^2}–C_{sp^2}$, etc. [13]. Similarly a second added constants data set, ARET-DIS.STO, was created from the main parameters of Table 1 to which was added the last subsection [14] for use with disilenes. These files in Fortran code followed the "Added Constants if NCONST .ne.0" format given in the manuals for PF or PCMODEL.

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[13] The prefix ARET in the name of the added constants data file causes the program to recognize that C_{ar} (atom type 40) must be distinguished from C_{sp^2} (atom type 2).

[14] Copies of the two data files ARET-SIL.STO and ARET-DIS.STO will be provided by either of the authors on receipt of a self-addressed mailing envelope containing a 5.25 inch floppy disk.

[15] While the preliminary communication (Ref. 5a) mentioned the presence of toluene in the crystal lattice, the location of the toluene is not shown in the ORTEP diagram given in the main publication (Ref. 5b).

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