

Conformational behavior and electronic structure of silylketenes studied with quantum chemical calculations and photoelectron spectroscopy

Heidi M. Muchall, Nick H. Werstiuk, Jiangong Ma, Thomas T. Tidwell, and Kuangsen Sung

Abstract: The He(I) photoelectron spectra of silylketenes ($\text{Me}_3\text{Si}_2\text{C}=\text{C}=\text{O}$ (**1**), $\text{Me}_3\text{Si}_2\text{CH}=\text{C}=\text{O}$ (**2**), $\text{Me}_2\text{Si}(\text{CH}=\text{C}=\text{O})_2$ (**3**), $\text{MeSi}(\text{CH}=\text{C}=\text{O})_3$ (**4**), $(\text{SiMe}_2\text{CH}=\text{C}=\text{O})_2$ (**5**), and $(\text{CH}_2\text{SiMe}_2\text{CH}=\text{C}=\text{O})_2$ (**6**)) have been recorded and their structures and orbital energies have been calculated by ab initio methods. Orbital energies for disilanes **2** and **5** are strongly dependent on a Si-Si-C-C torsional angle due to $\sigma-\pi$ orbital interaction. Comparisons between experimental and simulated spectra show that **2** and **5** prefer conformations in which the Si-Si bond and ketene group(s) are approximately orthogonal (113° and 111° , respectively). Silylalkenes $\text{Me}_3\text{Si}_2\text{CH}=\text{CH}_2$ (**7**) and $(\text{SiMe}_2\text{CH}=\text{CH}_2)_2$ (**8**), which have been included in the computational study, show the same behavior as their corresponding silylketenes. Silylbis- and trisketenes **3-6** do not exhibit $\pi-\pi$ interaction of any significance. For Si-Si containing compounds, the best agreement between experimental and computed data was obtained when Becke3LYP/6-31G*//HF/3-21G* was employed.

Key words: conformational behavior, electronic structure, photoelectron spectroscopy, quantum chemical calculations, silylketenes.

Résumé : On a déterminé les spectres photoélectroniques He(I) des silylcétènes ($\text{Me}_3\text{Si}_2\text{C}=\text{C}=\text{O}$ (**1**), $\text{Me}_3\text{Si}_2\text{CH}=\text{C}=\text{O}$ (**2**), $\text{Me}_2\text{Si}(\text{CH}=\text{C}=\text{O})_2$ (**3**), $\text{MeSi}(\text{CH}=\text{C}=\text{O})_3$ (**4**), $(\text{SiMe}_2\text{CH}=\text{C}=\text{O})_2$ (**5**) et $(\text{CH}_2\text{SiMe}_2\text{CH}=\text{C}=\text{O})_2$ (**6**)) et on a calculé leurs structures et leurs énergies orbitales par des méthodes ab initio. Les énergies orbitales des disilanes **2** et **5** dépendent fortement d'un angle de torsion Si-Si-C-C dû à une interaction $\sigma-\pi$. Des comparaisons entre les spectres expérimentaux et simulés montrent que les composés **2** et **5** adoptent préférentiellement des conformations dans lesquelles la liaison Si-Si et le(s) groupe(s) cétène(s) sont approximativement orthogonaux (113° et 111° respectivement). Les silylalcènes $\text{Me}_3\text{Si}_2\text{CH}=\text{CH}_2$ (**7**) et $(\text{SiMe}_2\text{CH}=\text{CH}_2)_2$ (**8**) dont on a aussi calculé les énergies présentent le même comportement que celui des silylcétènes correspondants. Les silylbis- et triscétènes **3-6** ne présentent pas d'interactions $\pi-\pi$ significatives. Pour les composés comportant une liaison Si-Si, l'utilisation de la méthode Becke3LYP/6-31G*//HF/3-21G* conduit au meilleur accord entre les données expérimentales et calculées.

Mots clés : comportement conformationnel, structure électronique, spectroscopie photoélectronique, calculs quantiques de chimie, silylcétènes.

[Traduit par la rédaction]

Introduction

Studies on ketenes have shown a remarkable stabilizing effect of silyl substituents on the ketene group, giving persistent mono- and bisketenes (**1**). In a previous study (**2**), the availability of a number of conformationally flexible silylketenes had prompted us to employ photoelectron (PE) spectroscopy,

the technique giving information about bonding in organic molecules. PE spectroscopy has been of continued use for conformational analyses where orbital energies depend on torsional angles (**3**) and has proved especially suited for systems with neighboring electron lone pairs or π electrons. Besides the expected $\pi-\pi$ interaction in the bisketenes studied, ab initio calculations suggested an interesting $\sigma-\pi$ interaction in *t*-BuMe₂SiCH=C=O involving an energetically high-lying orbital of the *tert*-butylsilyl bond (**2**). Using Koopmans' theorem (**4**) to correlate HF ab initio orbital energies and experimental ionization potentials, we interpreted and accurately simulated the experimental PE spectra, thereby confirming the applicability of the combination of ab initio calculations and PE spectroscopy to the study of the conformational behavior of silylketenes. PE spectra of disilanes (**5**) and ketenes (**6**) are well known, yet there are no spectra reported of compounds combining disilane and ketene moieties, compounds of potential interest with respect to $\sigma-\pi$ orbital interactions. Further-

Received June 20, 1997.

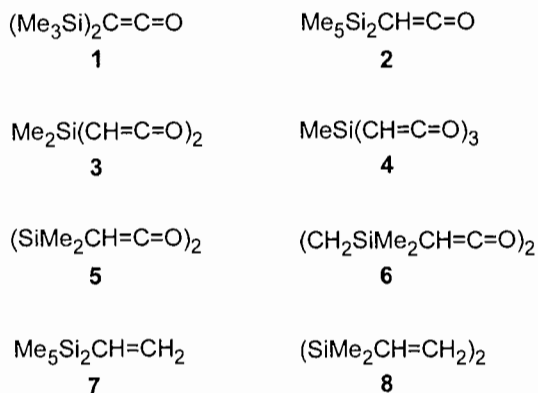
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more, while we presented PE spectra of some silylketenes and silylbisketenes (2), there are no reports of such studies of compounds having more than one ketene group connected to a silicon atom, which are sources of possible remote π - π orbital interactions.

The preparation of such compounds has been reported recently (7, 8), and in this paper we report the conformational behavior of silylketenes **1**-**6** using *ab initio* calculations and PE spectroscopy. Where necessary for the interpretation of the experimental spectra, Becke3LYP (9) of density functional theory (DFT) has been employed alongside HF (10) theory.² Computational studies for silylalkenes **7** and **8** are included for comparison. The ionization potentials of these species have been presented (12) but representations of their PE spectra have not been reported. The interpretation of the spectra for **7** and **8** (12) does not agree with our conclusions on similar systems (2), and so we have studied **7** and **8** in more detail computationally.



Experimental

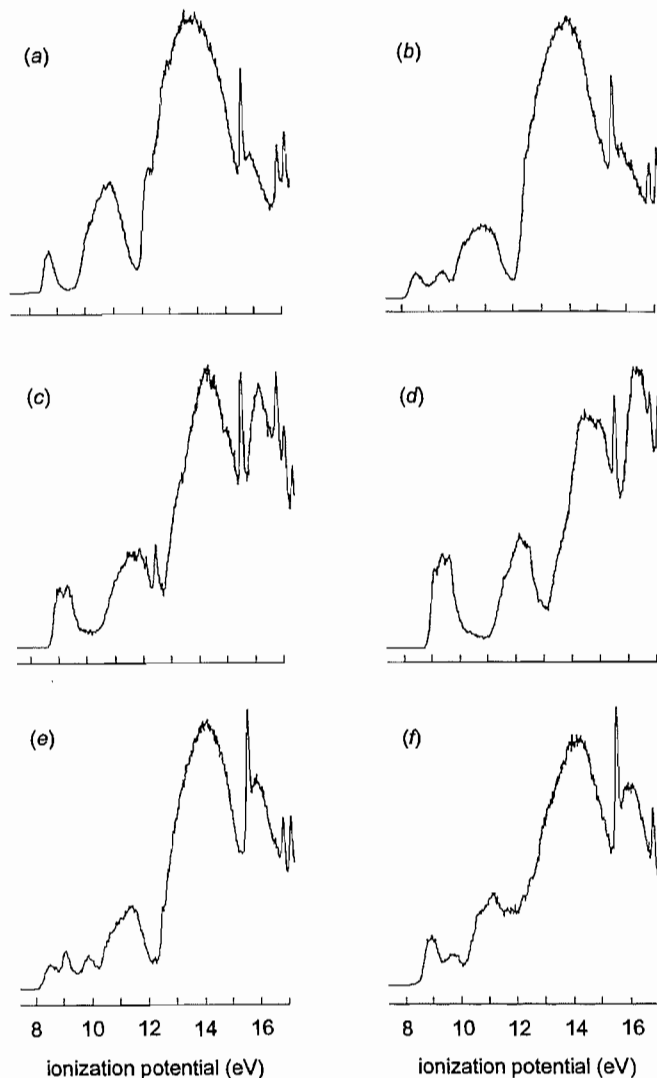
Ab initio HF (10) and Becke3LYP (9) calculations were carried out on IBM RS/6000 model 39H, 350, and 530 computers with GAUSSIAN 94 (13).³ Semiempirical PM3 (14) calculations were performed with the MOPAC (15) program package (version 6.00) on an IBM RS/6000 model 320H computer. Except for those dihedral angles fixed in torsional analyses and indicated in the text, all geometry parameters were optimized. Synthetic spectra were calculated from the MO results with a Fortran program PESPEC (16). Graphical representations of the computationally determined eigenvectors (PM3//HF/3-21G*; these were checked against HF/3-21G*//HF/3-21G* as well as Becke3LYP/6-31G*//HF/3-21G* eigenvectors and were found to compare well) were plotted from HyperChem 4.⁴

² A rationale for the successful application of the Koopmans' theory-like interpretation of the orbital energies obtained at the DFT level of theory in a PE spectroscopic study of a series of carbenes has recently been provided by Arduengo et al. (11). It is clear that applying a uniform shift based on the difference in calculated HOMO energy and the experimental first vertical IP to the DFT orbital energies nicely reproduces the PE spectra of compounds presented here, which are vastly different from the carbenes studied by Arduengo.

³ Total energies are uncorrected; for a discussion of the inclusion of zero-point vibrational energies in these studies, see Werstuijk et al. (2).

⁴ Hypercube, Inc., Waterloo, Ont. 1994.

Fig. 1. UV photoelectron spectra of silylketenes (a) **1**, (b) **2**, (c) **3**, (d) **4**, (e) **5**, and (f) **6**.



He(I) PE spectra were measured with a locally built instrument (17) by signal averaging 40-50 scans, with nitrogen (15.6 eV) as the calibrant. Linearity of the scale was ensured through calibrations with methyl iodide (9.54 and 10.16 eV) and O₂ (12.30 eV) performed prior to the experiments.

Silylketenes **1**-**6** were synthesized as reported (7, 8).

Calculations and photoelectron spectra

Bis(trimethylsilyl)ketene (1)

Except for the rotation of the two trimethylsilyl groups, there is no conformational flexibility in this simple silylketene. According to HF/3-21G*, the preferred conformation **1a** has C₂ symmetry, one methyl group of each Me₃Si moiety being twisted out of the *syn*-periplanar (*sp*) arrangement with the ketene group by 17.7° to avoid eclipsing. Fixing these torsional angles at 0° (*sp* conformation **1b**) leads to an increase in total energy of 2.90 kJ mol⁻¹, whereas keeping them at 180° (*anti*-periplanar conformation **1c**) causes a destabilization of 18.49 kJ mol⁻¹. Neither **1b** nor **1c** are minima on the potential energy surface with HF/3-21G*.

Table 1. Selected experimental vertical ionization potentials IP (eV) and calculated orbital energies ϵ (eV) of silylketenes **1–6** and silylalkenes **7** and **8**.

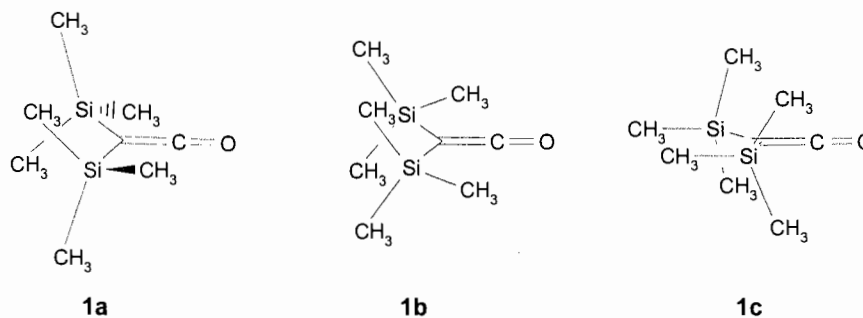
	IP	$-\epsilon^a$		
		HF/3-21G*//HF/3-21G*	PM3//HF/3-21G*	B3LYP/6-31G*//HF/3-21G*
1	8.75	9.24	8.52	6.18
	10.2	11.23	9.93	7.81
2^b	8.52	8.92	8.36	6.00
	9.51	10.42	9.69	7.20
	10.2	11.53	10.44	7.96
3	9.10	9.56	8.90	6.47
	9.38	9.81	9.10	6.64
	10.9	12.34	11.06	8.69
4	9.12	9.73	8.97	6.64
	9.42	9.96	9.14	6.80
	9.61	9.96	9.14	6.80
	11.6	13.08	11.56	9.35
5	8.52	8.75	8.17	5.93
	9.10	9.82	9.21	6.64
	9.88	10.95	10.08	7.64
	10.5	11.84	10.59	8.25
6	8.9	9.26	8.74	6.20
	8.9	9.60	8.99	6.46
	9.73	10.90	9.95	7.53
	10.6	11.90	10.59	8.31
7	8.56 ^c	9.11	8.67	6.32
	10.0 ^c	10.55	10.15	7.43
8^d	8.63 ^c	8.90	8.59	6.22
	10.0 ^c	10.25	10.11	7.29

^aGiven for the most stable conformer according to HF/3-21G*.

^bOrbital energies are given for conformer **2a**.

^cReference 12.

^dOrbital energies are given for conformer **8b**.



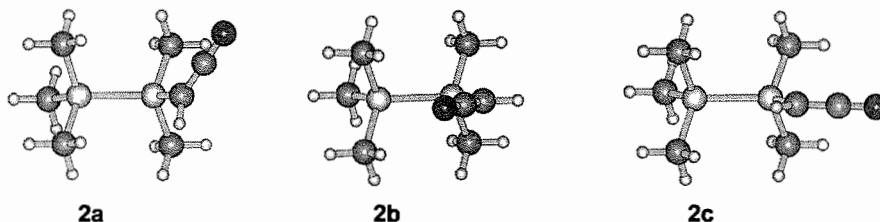
The HOMO of **1**, which is mainly π_{CCO} with only minor contributions from Si—CH₃ bonds, is followed by a group of five orbitals (HOMO-1 to HOMO-5; 11.23, 11.73, 11.84, 12.07, and 12.12 eV), all of which have σ Si—C character. Upon rotation of one trimethylsilyl group, there is essentially no dependence of the orbital energies on the torsional angle.

The PE spectrum of ketene **1**, which resembles that of Me₃SiCH=C=O (**2**), exhibits two separate bands in the low-energy region (Fig. 1(a)). The first band (8.75 eV) belongs to just one ionization, the second, centered at 10.7 eV, to five.

Another band at 12.29 eV is resolved in front of the σ region. Compared to the first ionization of Me₃SiCH=C=O (8.95 eV) (**2**), that of **1** is shifted to a slightly lower IP, showing the destabilization of the π_{CCO} -HOMO due to further SiMe₃ substitution. The relative positions of the bands correspond well to the computed relative orbital energies for **1** (Table 1); in particular, the HOMO energy taken from a PM3 single-point calculation on the HF/3-21G* optimized geometry of 8.52 eV is very close to the experimental value of 8.75 eV for the first ionization.

Table 2. Calculated total (hartrees) and relative (kJ mol^{-1}) energies of conformers of silylketenes **2–6** and silylalkenes **7** and **8**.

	HF/3-21G*//HF/3-21G*		Becke3LYP/6-31G*//HF/3-21G*	
	Total energy	Relative energy	Total energy	Relative energy
2a	-922.371 105	0.73	-930.634 892	0.00
2b	-922.371 385	0.00	-930.634 682	0.55
2c	-922.369 523	4.88	-930.632 989	4.99
3a	-666.976 824	0.00	-673.387 789	1.53
3b	-666.976 810	0.04	-673.388 374	0.00
3c	-666.975 340	3.89	-673.387 614	1.99
4a	-777.897 465	0.00	-785.486 598	0.00
4b	-777.896 452	2.66	-785.486 226	0.98
4c	-777.895 114	6.17	-785.485 459	2.99
5a	-1033.290 507	0.00	-1042.733 900	0.00
5b	-1033.290 475	0.08	-1042.733 897	0.01
5c	-1033.286 794	9.74	-1042.729 943	10.38
5d	-1033.290 172	0.88	-1042.733 053	2.22
6a	-1110.951 768	0.00	-1121.368 596	0.00
6b	-1110.951 752	0.04	-1121.368 400	0.51
6c	-1110.951 559	0.55	-1121.368 461	0.35
7a	-849.081 419	0.00	-856.610 379	0.00
7b	-849.080 692	1.91	-856.609 137	3.26
8a	-886.711 307	0.00	-894.685 432	0.76
8b	-886.711 296	0.03	-894.685 723	0.00

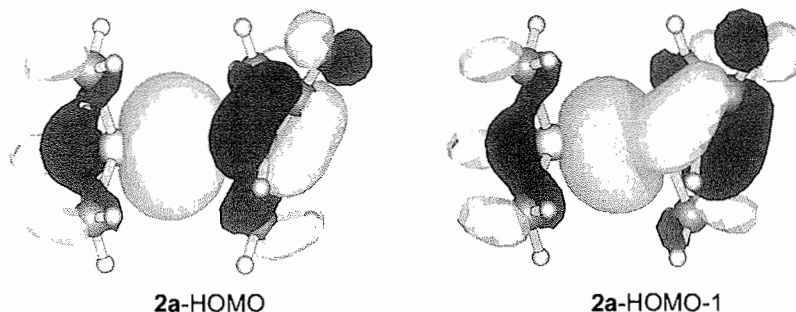
**(Trimethylsilyldimethylsilyl)ketene (2)**

The most stable conformation of the related (*tert*-butyldimethylsilyl)ketene was found to be one in which one methyl group is oriented *sp* to the ketene group, the $\text{Bu}^t\text{-Si-C-C}$ dihedral angle being 115.4° (2). We studied three conformations, **2a–2c**, of disilylketene **2**. While HF/3-21G* calculations predict the 0° conformer (Si-Si-C-C torsional angle) **2b** to be lowest in energy, both HF/6-31G*//HF/3-21G* and Becke3LYP/6-31G*//HF/3-21G* calculate **2a** to be more stable than **2b**, the 180° conformer **2c** showing the highest energy (Table 2). For *t*-BuMe₂SiCH=C=O the conformation analogous to **2a** was also found to be most stable (2). In **2a**, the Si—Si bond length is 234.7 pm and the Si-Si-C-C dihedral angle is 112.6° . The semiempirical PM3 method stretches the Si—Si bond considerably (to 246.0 pm in the optimized **2a**), which allows the ketene group to adopt a smaller torsional angle of 92.5° .

The geometries of **2** and (*tert*-butyldimethylsilyl)ketene are comparable but there is a distinct difference in their electronic structures. In the *tert*-butyl carbon analog of **2**, orbital energies do not seem to be a function of the $\text{Bu}^t\text{-Si-C-C}$ torsional angle (2). For **2a**, HOMO and HOMO-1 are the antisymmetrical and symmetrical combinations of π_{CCO} with σ -type contribution

of electron density on the Si—Si bond. HOMO-1 is followed by a group of four orbitals (HOMO-2 to HOMO-5, σ Si—C type, values not given) that are energetically close together. In disilane **2**, the HOMO/HOMO-1 splitting is strongly dependent on the Si-Si-C-C torsional angle, regardless of the level of theory applied. HOMO (σ_{SiSi}) and HOMO-1 (π_{CCO}) show no mixing and are quite similar in energy in the 0° conformer **2b**, $\Delta\epsilon$ of these two orbitals being 0.33 (PM3), 0.27 (HF/3-21G*), and 0.42 eV (Becke3LYP/6-31G*//HF/3-21G*). This difference grows as the torsional angle is increased and the orbitals are allowed to mix. The greatest $\Delta\epsilon$ of 1.73 (PM3), 1.63 (HF/3-21G*), and 1.28 eV (Becke3LYP/6-31G*//HF/3-21G*), due to maximal σ - π interaction, is found at 90° , decreasing again to about the 0° value on going to 180° . An explanation for the preference of a dihedral near 90° (**2a** is the global minimum) in spite of this destabilizing interaction is given by the very low lying LUMO of σ^*_{SiSi} character: the $\sigma^*-\pi$ interaction is stabilizing.

The potential for this twisting about the Si—CCO bond was obtained by fixing the Si-Si-C-C dihedral at 0° , 45° , 90° , 135° , and 180° and relaxing the rest of the molecule. Fitted curves as calculated by PESPEC (16) on HF/3-21G* and Becke3LYP/6-



31G**//HF/3-21G* relative energies are shown in Fig. 2(a). The change in orbital energies of the four highest occupied molecular orbitals upon increase of the Si-Si-C-C torsional angle is given in Fig. 3(a) (Becke3LYP/6-31G**//HF/3-21G* values). The progression of HOMO and HOMO-1 clearly shows the pronounced σ - π interaction in disilane **2** that was previously proposed on the basis of UV data for **2** (8).

In the PE spectrum of disilylketene **2** depicted in Fig. 1(b), the first (8.52 eV) and second (9.51 eV) ionization each give rise to a separate band; the third band (centered at 10.9 eV) is formed by four ionizations. The overall appearance of the spectrum is similar to that of (*tert*-butyldimethylsilyl)ketene (**2**), yet the first IP of **2** is found at a lower value than that of the corresponding *tert*-butyl carbon analog (8.79 eV), which indicates a greatly destabilized HOMO. This and the experimentally determined gap of 1 eV between the first two ionizations of **2** shows the extent of interaction between σ_{SiSi} and π_{CCO} in **2**, which was predicted by the calculations (Fig. 3(a)). While both HF/3-21G**//HF/3-21G* and HF/6-31G**//HF/3-21G* overestimate the σ - π interaction, leading to an exaggerated splitting of the first two orbitals, there is excellent agreement between the relative ionization energies and the relative calculated orbital energies of **2** when Becke3LYP is employed. Electron correlation, therefore, cannot be neglected when describing the electronic structure of this disilane. The simulated PE spectrum obtained with PESPEC and based on the calculated potential (Fig. 2(a)) is given in Fig. 4(a). Twelve eigenvalues (HOMO to HOMO-11) were used to synthesize the partial spectrum of **2**, convoluted with a Gaussian lineshape with a full width at half height (FWHM) of 0.4 and the temperature set at 300 K. The simulated spectrum correctly reproduces the low-energy part of the experimental spectrum of **2**, suggesting that disilylketene **2** prefers a conformation in which the Si-Si bond and ketene group are close to orthogonal for maximum orbital interaction. While Becke3LYP values are excellent in terms of relative orbital energies, they differ by several eV from the experimental values.² As for **1**, the energy of the first ionization can be predicted well using PM3//HF/3-21G*.

(Trimethylsilyldimethylsilyl)ethene (**7**)

A comparison of (*tert*-butyldimethylsilyl)ketene and (*tert*-butyldimethylsilyl)ethene revealed similar conformational behavior and orbital interactions, with more σ - π interaction for the alkene as judged by the angular dependence of the HOMO/HOMO-1 gap (2). Khvostenko et al. (12) reported an absence of σ - π conjugation for (trimethylsilyldimethylsilyl)ethene (**7**) based on the first IP in the PE spectra of the

Fig. 2. Torsional potential calculated with PESPEC (HF/3-21G*, solid line; Becke3LYP/6-31G**//HF/3-21G*, broken line): twisting about (a) the Si-CCO bond of **2**, (b) one Si-CCO bond of **5**, and (c) the CH₂-CH₂ bond of **6**.

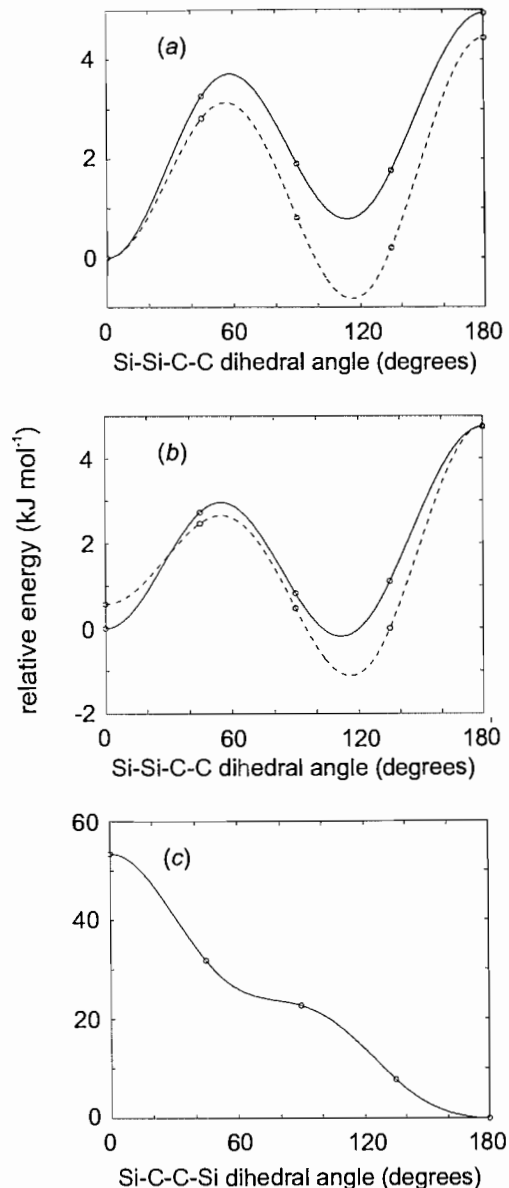
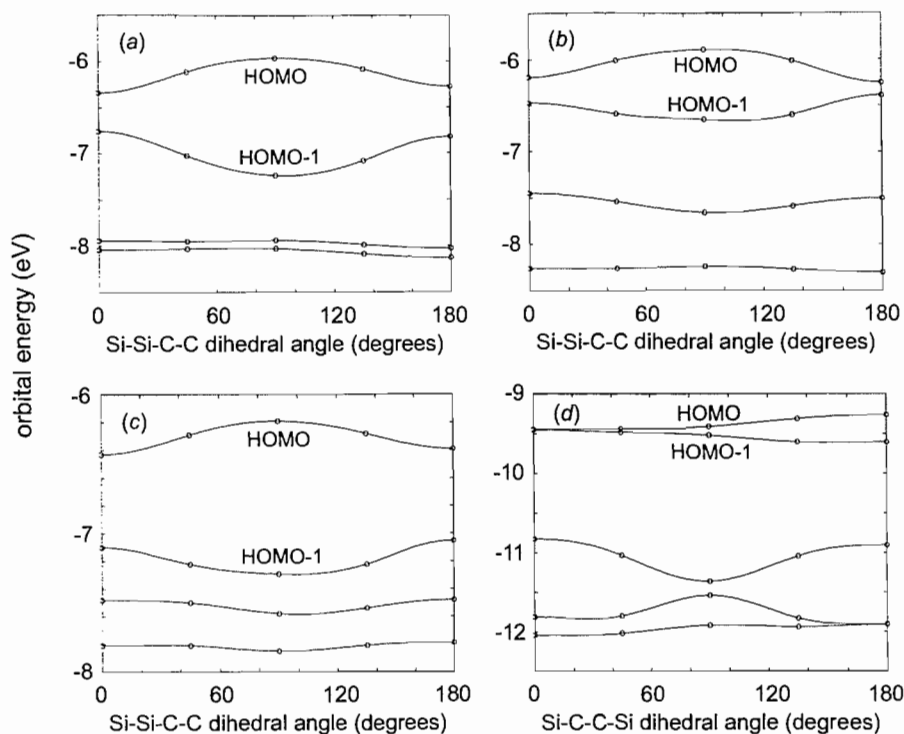


Fig. 3. Angular dependences of the MO energies of HOMO to HOMO-3 of (a) **2**, (b) **5**, and (c) **8** (Becke3LYP/6-31G*//HF/3-21G*), as well as (d) HOMO to HOMO-4 of **6** (HF/3-21G*).



series **7** (8.56 eV), 1,2-divinyl-1,1,2,2-tetramethyldisilane (**8**) (8.63 eV), and hexamethyldisilane (8.69 eV), which they claimed to be constant. As this was quite unexpected, we calculated the potential for the rotation of the ethylene moiety in alkene **7**. Two conformations, **7a** and **7b**, correspond to **2a** and **2b**, respectively. The Si—Si bond length (235.0 pm) and Si—Si—C—C dihedral angle (109.4°) in the optimized **7a** (HF/3-21G*) compare to those in **2a**, as do the orbitals (LUMO of **7a** is a low-lying σ^*_{SiSi} , HOMO the antibonding combination of σ_{SiSi} with $\pi_{\text{C=C}}$). Likewise, the Becke3LYP/6-31G*//HF/3-21G* fitted potential for the rotation in **7** resembles that found for **2**, except for the energy difference of 3.26 kJ mol⁻¹ between **7a** and the 0° conformation **7b** being larger than for the respective conformations of **2** (0.73 kJ mol⁻¹). This is due to the greater steric interaction experienced by the vinyl hydrogen atom, which points inwards in **7**, compared to that for the ketene group in **2** and can be seen in the different Si—C—C angles (122.7° **2a**/125.2° **7a**, 121.2° **2b**/125.9° **7b**), as for the *tert*-butyl analogs (**2**). Yet in contrast to these *tert*-butyl compounds, the σ — π interaction seems to be greater in ketene **2** (the HOMO/HOMO-1 gap increasing from 0.42 to 1.28 eV) than in alkene **7** (from 0.50 to 1.18 eV, Becke3LYP/6-31G*//HF/3-21G*, plot not shown). The torsional dependence of HOMO and HOMO-1 resulting from the relative orientations of the Si—Si bond and the C—C double bond in alkene **7** is clearly in contrast to the absence of σ — π conjugation published by Khvostenko et al. (12). The simulated PE spectrum for **7** (Becke3LYP/6-31G*//HF/3-21G*, 12 eigenvalues, FWHH 0.4, temperature 300 K), which unfortunately cannot be compared to the experimental spectrum, is shown in Fig. 4(b). Yet it was stated (12) that the second and the third band in

the spectrum of **7** are poorly resolved and this is correctly reproduced by the calculations as can be seen in the synthesized spectrum. Thus we can conclude that alkene **7** exhibits the same conformational properties as ketene **2**.

Dimethylsilylbisketene (**3**)

Five conformations of bisketene **3** were studied at the ab initio level. Conformer **3a**, shaped like a partial propeller (where one “blade” is represented by a methyl group) with one ketene group *sp* to the other Si—CCO bond and one ketene group *sp* to one Si—CH₃ bond (the torsional angles being 12.6° and 5.2°, respectively), and conformer **3b**, another propeller, with C₂ symmetry and ketene groups each *sp* to one Si—CH₃ bond (OC—C—Si—CH₃ dihedrals are 4.2°) and *anti* with respect to each other, are essentially equal in energy at HF/3-21G*. The related *syn* conformer **3c** with ketene groups *sp* to the same Si—CH₃ bond (OC—C—Si—CH₃ dihedrals are 8.4°) is 3.9 kJ mol⁻¹ higher in energy (Table 2). While HF/6-31G*//HF/3-21G* total energies of the three conformers (not given) follow the same ordering, Becke3LYP/6-31G*//HF/3-21G* reverses the energetic order of **3a** and **3b**. Two in-plane conformations (U and W shaped), which are still higher in energy at the semiempirical level (PM3), are not stationary points according to ab initio calculations.

Orbital energies for the three low-energy conformations **3a–3c** are very similar, according to all computational methods applied. HOMO and HOMO-1 (symmetrical and antisymmetrical combinations of π_{CCO} 's) are close in energy, followed by a group of three orbitals (HOMO-2 to HOMO-4, values not given) that are mainly σ Si—C type. To obtain the potential energy surface and determine the extent of orbital

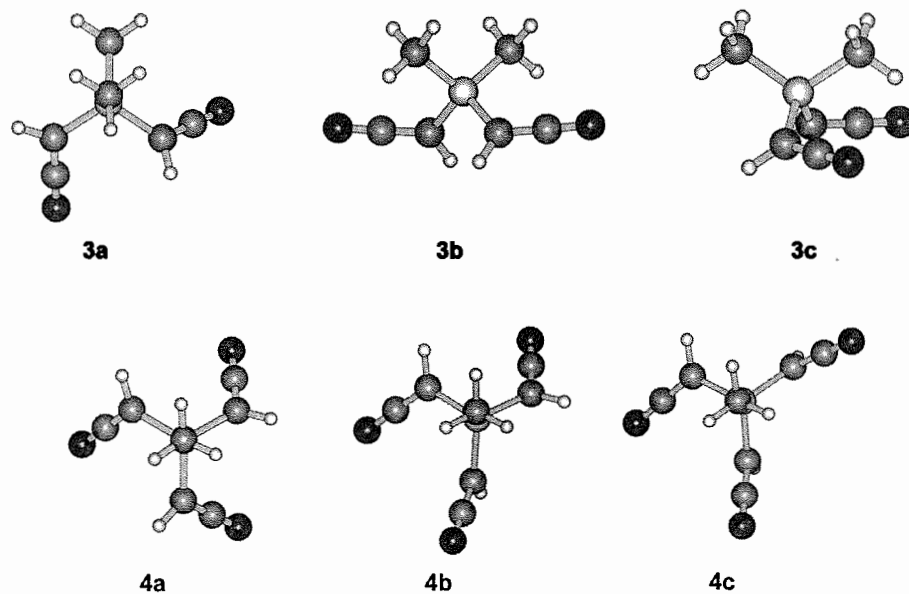
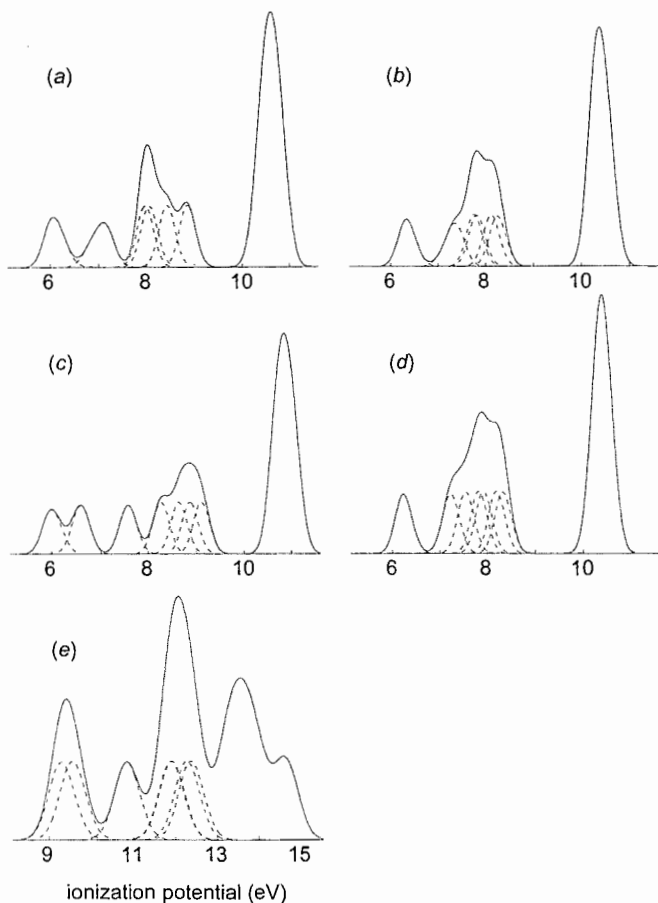


Fig. 4. Synthetic partial UV photoelectron spectrum calculated with PESPEC of (a) 2, (b) 7, (c) 5, (d) 8, and (e) 6.



energy dependence on changes in the orientation of the two ketene groups, one dihedral (of the ketene group *sp* to the Si—CH₃ bond) was restrained at its original value and the other varied (plots not shown). As suggested by the similar energies

of HOMO and HOMO-1 of 3a–3c, the orbital energies are almost independent of the torsional angle. This fact, as well as the near degeneracy of HOMO and HOMO-1, shows that there is little π – π interaction between the two ketene moieties in bisketene 3.

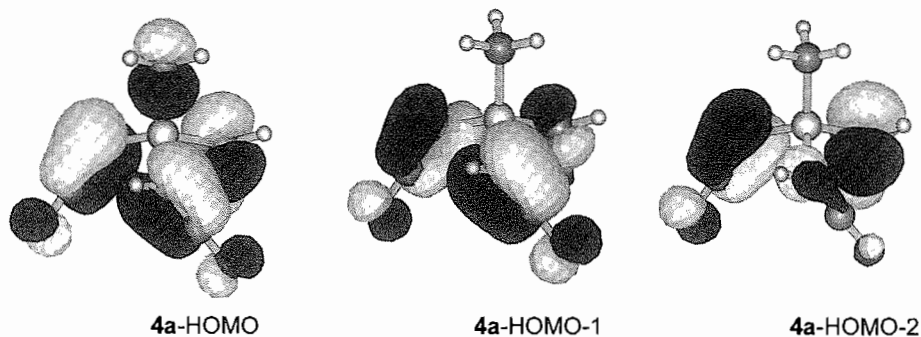
Like 1, the PE spectrum of bisketene 3 (Fig. 1(c)) closely resembles that of Me₃SiCH=C=O (2). For 3, the first band is made up of two ionizations (9.10 and 9.38 eV) and the second, centered at 11.7 eV, corresponds to three (the sharp peak at 12.51 eV is due to traces of water). The stabilization of the HOMO (and therefore greater value for the first IP), upon substitution of one methyl group in Me₃SiCH=C=O by a second ketene moiety, and the very small splitting of the first two ionizations arising from the absence of significant π – π interaction are accurately predicted by the calculations (Table 1).

Methylsilyltrisketene (4)

The most stable conformation of trisketene 4 is the symmetrical propeller 4a, as found with all computational methods (Table 2). All ketene groups in 4a are oriented *sp* to a Si—CCO bond; the respective torsional angles OC-C-Si-CCO are 10°. Two further low-energy conformations 4b and 4c can be derived from the propeller 4a by twisting one or two ketene groups, respectively, into an arrangement *sp* to the Si—CH₃ bond.

Molecular orbitals HOMO to HOMO-5 for 4a–4c come in two groups of three centered around 9.8 and 13.2 eV as calculated by HF/3-21G*. The first group is made up of three combinations of three π_{CCO} 's, one symmetrical and two antisymmetrical. The energy difference $\Delta\epsilon$ between the first (HOMO) and last (HOMO-2) orbital in this group is 0.23 (4a), 0.53 (4b), and 0.67 eV (4c). In 4a, HOMO-1 and HOMO-2 are degenerate because of the symmetry of the conformer; as the orbitals split in 4b and 4c, $\Delta\epsilon$ becomes bigger. Orbitals in the second group (HOMO-3 to HOMO-5) are three combinations of σ Si—C type and show a similar behavior to those of the first group with respect to $\Delta\epsilon$.

For the determination of the potential energy surface (plot not shown), two ketene dihedrals in 4a were kept at their original values while the remaining one was twisted. Again, as in



the case of dimethylsilylbis ketene (**3**), the orbital energy dependence on the torsional angle is small, further confirming the lack of significant π - π interaction between the ketene groups in these molecules.

The PE spectrum of trisketene **4**, which on going from $\text{Me}_3\text{SiCH}=\text{C}=\text{O}$ has two methyl groups replaced by ketene groups, shown in Fig. 1(d) resembles that of bis ketene **3**. For **4**, there are two bands of similar intensity in the low-energy region, one around 9.4 eV for which three maxima can be given, the other at about 12.2 eV. Each is composed of three ionizations. Again, this spectrum displays the computationally predicted small splitting of the first three IPs coherent with a small π - π interaction between the ketene groups (Table 1). The fact that we are able to assign three maxima in the first band suggests that **4** to a certain degree exists in unsymmetrical conformations that do not permit HOMO-1 and HOMO-2 to be degenerate.

1,2-Bis(ketenyl)-1,1,2,2-tetramethyldisilane (**5**)

Three conformations of disilylbis ketene **5** with the OCC-Si-Si-CCO dihedral at 180° were studied and, except for the semiempirical PM3 method, all calculations predict **5a** to be lowest in energy (Table 2). Ketene groups in the C_2 symmetrical **5a** are oriented *sp* to Si- CH_3 bonds (C-Si-C-C dihedral is 9°) and *syn* towards each other. The corresponding *anti* conformer **5b**, which is the global minimum with PM3, is only slightly destabilized. Conformer **5c** with Si-Si-C-C dihedral angles at 180° is higher in energy. The Si-Si bond length (234.2 pm) and Si-Si-C-C torsional angles (111.0°) of **5a** obtained with HF/3-21G* resemble those of **2a**, the other disilane studied. Again, PM3 lengthens the Si-Si bond to 246.7 pm, which allows the ketene groups to approach the optimal right angle. The fourth conformation studied with ab initio methods, **5d**, differs from the other three in that the OCC-Si-Si-CCO dihedral is at 65.3° . Conformer **5d** is lower in energy than **5c** (Table 2).

As was the case for disilylketene **2**, there is a pronounced difference in orbital energies for conformers **5a** and **5c** that is once more indicative of a σ - π interaction. For **5a** with the Si-Si bond and ketene groups near orthogonal (ab initio calculations), HOMO to HOMO-2 are more or less equally spaced orbitals followed by a group of four (mainly σ Si-C character). HOMO and HOMO-2 show a symmetrical combination of π_{CCO} 's with σ contribution of electron density on the Si-Si bond ($\pi_{\text{CCO}}^+/\sigma_{\text{SiSi}}$); HOMO-1 is the antibonding combination of π_{CCO} 's (π_{CCO}^-). As for disilylketene **2**, the LUMO is a low-lying σ_{SiSi}^* . In the "stretched" **5c**, HOMO and

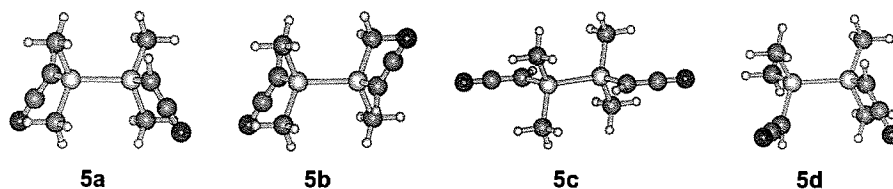
HOMO-1 (π_{CCO}^- and π_{CCO}^+ , respectively) are almost degenerate, and HOMO-2 is the unperturbed σ_{SiSi} .

Conformers **5a-5d** suggest that there are three bonds in this disilane that should be included in a conformational study, one Si-Si and two Si-CCO bonds. To study this problem computationally, rotations about the Si-Si bond and one Si-CCO bond were examined separately. Neither total energy nor orbital energies depend on the OCC-Si-Si-CCO torsional angle (no plots shown) but the rotation of one ketene moiety has an effect on the orbital energies. For the calculation of the respective potential, one Si-Si-C dihedral was fixed at its optimized value⁵ and the other rotated through 0° , 45° , 90° , 135° , and 180° . The fitted potentials for HF/3-21G* and Becke3LYP/6-31G**/HF/3-21G* relative energies are shown in Figure 2(b). Figure 3(b) gives the Becke3LYP/6-31G**/HF/3-21G* eigenvalues for the four highest occupied molecular orbitals as a function of the torsional angle. To judge the extent of the effect of σ - π mixing on the orbital energies is not simple because of multiple interactions; UV spectra seem to indicate that it is smaller in bis ketene **5** than it is in monoketene **2** (8).

As is the case for bis ketene **3** and trisketene **4**, there is only a small π - π interaction in **5**. A simple "uncoupling" of π_{CCO}^+ and σ_{SiSi} , which form HOMO and HOMO-2, gives a π_{CCO}^+ that is in the energetic neighborhood of π_{CCO}^- . This is confirmed by isodesmic considerations on the unsubstituted bis(ketenyl)disilane ($\text{H}_2\text{Si}-\text{CH}=\text{C}=\text{O}$)₂ (**7**).

The PE spectrum of disilylbis ketene **5** (Fig. 1(e)) shows three bands (8.52, 9.10, and 9.88 eV) of comparable intensity belonging to one ionization each, followed by a broad band centered at 11.2 eV that is composed of four ionizations. The first band in the spectrum of **5** is found at the same low value as that for **2**, again indicating an interaction between σ_{SiSi} and π_{CCO} . As for **2**, the best simulated spectrum was obtained using the Becke3LYP/6-31G**/HF/3-21G* calculated surface and eigenvalues, which again shows the importance of including electron correlation in calculations of the electronic structure of disilanes. The synthesized partial PE spectrum based

⁵ The assumption that keeping the second dihedral at its optimized value would lead to correct results was drawn from the PM3 surface obtained for the rotation of *both* ketene groups of disilylbis ketene **5**. This hypersurface obtained from 25 points (0° , 45° , 90° , 135° , and 180°) suggests that conformations lying on the lowest energy path have one Si-Si-C-C dihedral angle at 90° . This is near the optimized PM3 value for this dihedral in **5a**.



on the 13 highest occupied molecular orbitals from PESPEC with a Gaussian convolution of 0.4 and a temperature of 300 K displayed in Fig. 2(c) is an excellent match of the experimental low-energy region in the spectrum of **5**. Like disilylketene **2**, disilylbisketene **5** prefers conformations in which its ketene moieties are arranged approximately orthogonal to the Si—Si bond to allow for maximum orbital interaction.

1,2-Divinyl-1,1,2,2-tetramethyldisilane (**8**)

We also performed a conformational analysis for disilane **8**, which according to Khvostenko et al. (12) does not exhibit σ – π interaction. Two low-energy conformers **8a** (ethylene groups *syn*) and **8b** (ethylene groups *anti*) correspond to **5a** and **5b**, respectively. With HF/3-21G*, **8b** is less stable than **8a** by 0.03 kJ mol⁻¹ (the HF/6-31G*//HF/3-21G* value is 0.22 kJ mol⁻¹), their geometries are similar to those found for disilane **5**: the Si—Si—C—C dihedral in **8a** is 110°, the C—Si—C—C dihedral is at 11°. Becke3LYP/6-31G*//HF/3-21G* predicts **8b** to be more stable by 0.76 kJ mol⁻¹. The fitted potential (Becke3LYP/6-31G*//HF/3-21G*, plot not shown) for the torsion about one Si—CC bond (with the other one kept at approx. 110°) resembles that for **5** except for energy differences in **8** being more pronounced: ΔE between the two minima in the plot for **5** is 1.5 (Fig. 6), for **8** it is 4.5 kJ mol⁻¹. This can be explained as was done for alkene **7**. The dependence of the orbital energies on the Si—Si—C—C dihedral in **8** can be seen in Fig. 3(c). Just as for disilylbisketene **5**, the HOMO of **8** (π_{CC}^+/σ_{SiSi}) is destabilized by about 0.2 eV on increasing the torsional angle from 0° to 90° while HOMO-1 and HOMO-2 are stabilized in both cases to about the same extent. This suggests that there are similar σ – π interactions in disilanes **5** (ketene substituents) and **8** (alkene substituents). The simulated PE spectrum of **8** (Becke3LYP/6-31G*//HF/3-21G*, 12

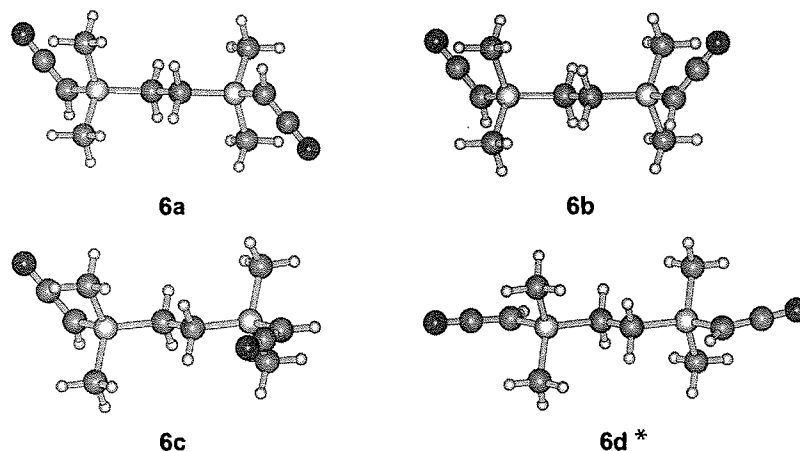
eigenvalues, FWHH 0.4, temperature 300 K) is shown in Fig. 4(d). Again, the experimental PE spectrum for **8** was not published but the stated poor resolution of the second and third bands (12) can be seen in the simulation.

1,2-Bis(ketenyl)dimethylsilyl)ethane (**6**)

According to HF/3-21G*, conformation **6a** with ketene groups *anti* and *sp* to the Si—CH₃ bonds (H₃C—Si—C—CO dihedral at 2.1°) is the global minimum. The related *syn* conformation **6b** is essentially equal in energy while **6c**, with one ketene group *sp* to a Si—CH₂ bond, is slightly destabilized by 0.55 kJ mol⁻¹ (Table 2). This energetic order is confirmed by HF/6-31G*//HF/3-21G* calculations whereas Becke3LYP/6-31G*//HF/3-21G* reverses the sequence of **6b** and **6c**, but all energy differences stay small. Conformation **6d**, which has both ketene groups *anti*-periplanar (*ap*) to the Si—CH₂ bonds, is the most stable conformation as determined by PM3, but is not a stationary point on the potential energy surface with HF/3-21G*.

HF/3-21G* HOMO to HOMO-6 orbital energies of **6a** come as groups of two (9.26 and 9.60 eV), one (10.90 eV), and four (11.90, 11.91, 12.28, and 12.37 eV), with the groups well separated. HOMO (π_{CCO}^+) and HOMO-1 (π_{CCO}^-) only show a small splitting. HOMO-2 has an in-phase electron contribution on the Si—CH₂ bonds and HOMO-3 is the antibonding combination of π_{CH_2} 's ($\pi_{CH_2}^-$) on the central C—C bond with electron density on the Si—CH₃ bonds. Orbital energies for **6a** and **6b** do not differ; for **6c** the HOMO/HOMO-1 splitting is smaller and the HOMO-2 is slightly raised.

Conformationally, bisketene **6** is the most complex of all the molecules studied. There are five important bonds here and the orbitals of **6** suggest that three of them, one CH₂—CH₂ and two Si—CCO bonds, could be of interest for an investiga-



* Representation of the PM3 geometry.

tion of orbital energy dependences. Again, the torsions about these bonds were examined separately. For the rotation about the central $\text{CH}_2\text{—CH}_2$ bond, the other four dihedral angles of the backbone of **6a** were kept at their optimized values and the Si-C-C-Si torsional angle was twisted through 0° , 45° , 90° , 135° , and 180° . Figure 2(c) shows the potential obtained from the calculated relative energies. Since **6** is a bisketene with an ethylene spacer, its potential is that of a 1,2-disubstituted ethane. The strong destabilization of the 60° conformation, which is obvious from Fig. 2(c), can be interpreted by the large direct interaction between the methyl groups of the two silicon substituents. From this potential, **6** is expected to be exclusively in a 180° conformation; the often-found 60° conformation of 1,2-disubstituted ethanes in the gas phase will not be occupied to a great extent.

Orbital energies of HOMO to HOMO-4 as a function of the central torsional angle are displayed in Fig. 3(d). The change of the Si-C-C-Si dihedral does not influence HOMO and HOMO-1 (π_{CCO} 's) significantly, which again is an indication of no $\pi\text{—}\pi$ interaction of any importance. HOMO-2 is lowest in energy at 90° and highest at 0° and 180° while HOMO-3 energies exhibit the opposite behavior. These two orbitals are almost degenerate in the 90° conformation, the point of avoided crossing, as can be seen in Fig. 3(d). They split to a maximum of about 1 eV as the dihedral is changed and, as a result of this, HOMO-2 moves up in energy and into the gap formed by HOMO/HOMO-1 and HOMO-3/HOMO-4 groupings.

In addition, the rotation about just one Si—CCO bond was examined, as in the case of disilane **5**. The remaining four dihedral angles of the backbone of **6a** were fixed at their optimized values. The potential obtained for twisting the $\text{CH}_2\text{—Si—C—C}$ torsional angle resembles that for **5** but the energy differences for **6** are smaller. This is reflected in the orbital energy dependence, which shows smaller changes but otherwise is the same as for **5** (plots not shown).

In the PE spectrum of bisketene **6** shown in Fig. 1(f), three bands are resolved from the main groups of the σ bands, belonging to two (8.9 eV), one (9.73 eV), and four (centered at 11.0 eV) ionizations. Even though the first band, which comprises ionizations from the two π orbitals (π_{CCO}^+ and π_{CCO}^-), shows individual maxima, they cannot be ascribed to discrete bands: a deconvolution would lead to a very small splitting. As for silylketenes **3**, **4**, and **5** bearing more than one ketene group, the $\pi\text{—}\pi$ interaction in **6** is almost nonexistent. The value of 8.9 eV for the first IP is close to that of (*tert*-butyldimethylsilyl)ketene (8.79 eV) (**2**), which indicates a similar destabilization of the ketene π orbital due to alkyl substitution, and no further interaction. The most prominent feature in the spectrum, in spite of its size, is the band at 9.73 eV. It is situated in an energy gap of about 1.5 eV made up by the larger bands. From Fig. 3(d) it is clear that HOMO-2 is destabilized enough for this only when the substituents on the ethane moiety are arranged *ap* (Si-C-C-Si torsional angle at 180° , the 0° conformation is a maximum, see Fig. 2(c)). There is remarkable agreement between the simulated partial spectrum for this torsion (HF/3-21G*, 11 eigenvalues, FWHH 0.7, temperature 300 K) as displayed in Fig. 4(e) and the experimental PE spectrum of **6**. Unlike the cases of disilanes **2** and **5**, using DFT values for **6** gives a similar simulation with no further improvement, which clearly shows that it is important to con-

sider electron correlation for silylketenes containing a Si—Si bond, while it can be neglected for silylketenes without a Si—Si bond. For the latter, it is sufficient to employ HF/3-21G**//HF/3-21G*. There is no change in the synthesized spectrum when the torsion of one ketene group is considered, emphasizing the lack of importance of this motion on the electronic structure of **6**.

Conclusion

The PE spectra presented for silylketenes **1–6** have been interpreted on the basis of the conformational flexibility of the molecules. Calculated energy differences between conformers are small and all are significantly populated. For disilanes **2** and **5**, whose orbital energies are a function of a Si-Si-C-C torsional angle, this seriously affects the PE spectra. Because of a strong $\sigma\text{—}\pi$ interaction, the preferred conformation for **2** and **5** is one in which the Si—Si bond and ketene group are approximately orthogonal. The same is true for the corresponding silylalkenes **7** and **8**, contrary to what has been reported (12). In contrast to the strong $\sigma\text{—}\pi$ interaction, there is no $\pi\text{—}\pi$ interaction of any significance in bis- and trisketenes **3–6**. While HF calculations describe the electronic structure of silylketenes **1**, **3**, **4**, and **6** well, this level of theory is not sufficient for disilanes **2** and **5**. For these Si—Si containing compounds, Becke3LYP must be employed for accurate representations of the experimental PE spectra.

Acknowledgment

Financial support by the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

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