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Conformation Properties of Buta-1,3-diene-1,4-diones (Bisketenes): Computational and Photoelectron Spectroscopic Studies

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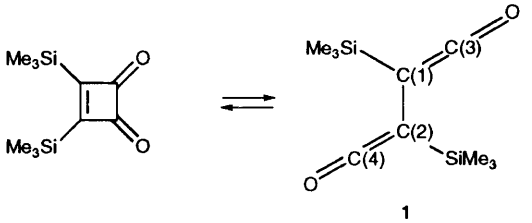
The highest occupied molecular orbital (HOMO) energies of a series of monoketenes RCH=C=O with a variety of representative substituents have been calculated by *ab initio* methods, and give good agreement with available experimental photoelectron ionization energies. The structures and orbital energies of the monoketenes $Me_3SiCH{=}C{=}O$ (**5**) and $Bu^tMe_2SiCH{=}C{=}O$ (**6**), the alkene $Bu^tMe_2SiCH{=}CH_2$ (**7**) and the bisketenes $(Me_3SiC{=}C{=}O)_2$ (**1**) and $(Bu^tMe_2SiC{=}C{=}O)_2$ (**4**) have also been calculated by *ab initio* methods, and are compared with experimentally measured photoelectron ionization energies. The spectra of the Bu^tMe_2Si compounds show a characteristic band associated with the $Bu^t{-}Si$ bond. Comparison of the measured and calculated spectra provides strong evidence that the bisketenes **1** and **4** exist predominantly in twisted conformations, with dihedral angles 105° in the former case and 120° in the latter. Dipole moment measurements on **1** and **5** confirm this conclusion.

The preparation of the unique stabilized and persistent bisketene, 2,3-bis(trimethylsilyl)buta-1,3-diene-1,4-dione (**1**) from thermolysis or photolysis of 3,4-bis(trimethylsilyl)cyclobut-3-ene-1,2-dione was recently reported [eqn. (1)][1a]. The reactivity of **1** has been studied experimentally,[1b] and the effect of substituents on the ring opening of **2** and the structures and stabilities of the resulting bis(ketene) conformations **3a–3c** (R = H, SiH_3, F) [eqn. (2)] have been examined by computational methods.[1c]



(1)

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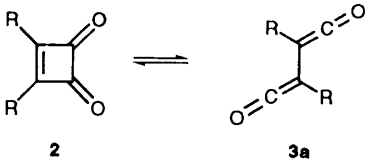
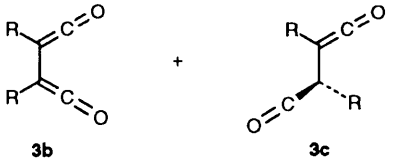


2 **3a**

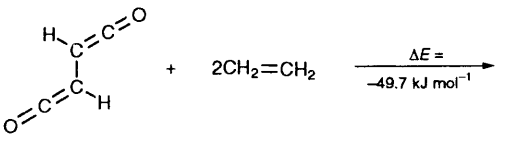


(2)

3b **3c**

These studies have shown that the strong ketene stabilizing effect of silyl substituents on monoketene[1d,e] is also manifested in bisketenes, although the effect of the substituents on the cyclobutenedione structure **2** influences the equilibrium as well.[1c] The parent bisketene structure **3a** (R = H) is also calculated to be destabilized relative to monoketenes, as illustrated by the calculated exothermic energy change of 49.7 kJ mol^{-1} in the isodesmic reaction of eqn. (3).

Photochemical decarbonylation is a characteristic reaction of ketenes and bisketenes[1a,b,f] and leads to alkynes in the case of **1** and **4**.[1a,b,f] Thermal decarbonylation of **1** and **4** has not been studied, but is not observed below 150 °C.



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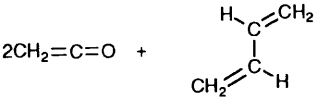
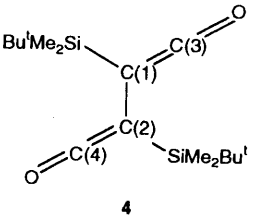


(3)

The availability of bisketene **1** and its analogue 2,3-bis(*tert*-butyldimethylsilyl)buta-1,3-diene-1,4-dione (**4**)[1b] as well as the monoketenes (trimethylsilyl)ketene (**5**) and (*tert*-butyldimethylsilyl)ketene (**6**) provided a unique opportunity to gain information on the bonding and conformational behaviour of silylketenes both by calculation, using *ab initio* theory, and experimentally by means of ultraviolet photoelectron (PE) spectroscopy. The study also is timely because the conformational properties of butadiene systems are topics of major current interest,[2,3] and PE spectroscopy has been of particular value in these investigations,[2] including examinations of silyl-substituted alkenes and dienes.[4] Reported herein are the results of theoretical and PE studies of **1**, **4**, **5**, **6** and (*tert*-butyldimethylsilyl)ethene (**7**). The alkene **7** was studied along with the ketenes in order to determine the behaviour of this *tert*-butyldimethylsilyl system relative to that of other silylalkenes,[4] including (trimethylsilyl)ethene, and for comparison of the effects of these two substituents with those on the ketenes.



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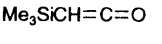

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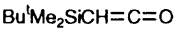

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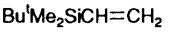

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Results and Discussion

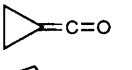
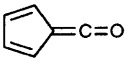
Calculations

The *ab initio* calculations on the ketenes **1**, **4**, **5**, **6** and the alkene **7** were carried out at McMaster University on IBM RS/6000 model 350 and 530 computers with GAUSSIAN 92.[5]† Because of the size of the molecules, the direct-SCF method was used in the calculations. The AM1 calculations were carried out at McMaster using AMPAC Version 2.10[6] running on an MIPS 2030 workstation. All optimizations were carried out using the keyword PRECISE to tighten the convergence criteria. Synthetic spectra were calculated from the MO results on a SUN 3/60 computer with a FORTRAN program PESPEC.[2c] The calculations on the monoketenes in Table 1 were carried out at the University of Toronto with the GAUSSIAN 90[7] and GAUSSIAN 92[5] series of programs running on Hewlett Packard 9000-750 and IBM RS/6000-530 computers.

Monoketenes

The orbital energies of the highest occupied molecular orbital (HOMO) of a series of monoketenes whose structures and energies were reported previously [1d–f] calculated at the HF/6-31G*//HF/6-31G* level are listed in Table 1 along with calculated and available experimental values of the ionization energy (E_i) of the HOMO.[8] The HOMO of these ketenes is the π_{CCO} of the ketenyl moiety. In the case of the mono-substituted ketenes the calculated MO eigenvalues (orbital energies) give calculated E_i values that are 0.1–0.48 eV higher than the experimental values, a result that is usually seen when eigenvalues based on Koopmans' theorem[9] are correlated with the experimental E_i.[10a] That the eigenvalues are higher than the E_i values has been attributed to the fact that electron correlation and molecular relaxation are not taken into account in the Hartree–Fock calculations.[10a] Even so, the orbital energies of $CH_2{=}C{=}O$, $CH_3CH{=}C{=}O$ and $CH(CN){=}C{=}O$ calculated at the HF/6-31G* level of theory reproduce the increase in the E_i of the HOMO found experimentally for the strong π-acceptor group CN.[8a] Thus these results permit for the first time the systematic evaluation of the effect of substituents on the ketene E_i. Many substituents give calculated values in the range of 9.1–9.9 eV (H, BeH, CH_3, NH_2, OH, F, MgH, AlH_2, SiH_3, PH_2 SH and Cl). Values outside this range include the strong π-acceptor groups BH_2, $CH{=}O$, CO_2H, $C{\equiv}N$ and NO_2, which have E_i values between 10.24 and 11.35 eV, and would stabilize the HOMO. A discussion of the importance of π-acceptor effects in ketenes has been presented elsewhere.[1d] The calculated E_i of $CF_3CH{=}C{=}O$ (10.75 eV) is also quite high. This effect evidently arises from the strong σ-withdrawing effect of the CF_3 group which stabilizes the HOMO. Experimentally $(CF_3)_2C{=}C{=}O$ also has a high first E_i at 10.95 eV.[8h] This effect is not so great with the σ-acceptor F and Cl substituents, since these also act as π donors which are destabilizing.[1d] The very low E_i values for $LiCH{=}C{=}O$ and $NaCH{=}C{=}O$ (7.70 and 7.27 eV, respectively) reflect the high ionicity of the metal–carbon bonds, and the consequent high electron density of the ketenyl π system. The groups $CH_2{=}CH$, $HC{\equiv}C$, Ph and c-Pr are all below 9.0 eV. These groups can act as π donors and this effect is destabilizing to the HOMO. The only ketene bearing a strong σ-acceptor group that has been studied with PE spectroscopy is $ClCH{=}C{=}O$,[8a–c] and the stabilization of the HOMO of this ketene is reproduced by calculation at the HF/6-31G* level of theory. These trends follow the effects of substituents on the photoelectron spectra of substituted benzenes, in which the ionization energies of the HOMO generally increase with the electron-accepting ability of the substituent.[10b,c]

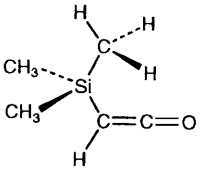
Table 1 Calculated (HF/6-31G*//HF/6-31G*) HOMO orbital energies (E_O) of ketenes (RCH=C=O) and calculated and observed first ionization energies (E_i/eV)

R	$-E_O/E_h$[a]	E_i(calc)/eV	E_i(obs)/eV	ref.
H	0.3584	9.75	9.64	8(*a*)
Li	0.2829	7.70		
BeH	0.3567	9.71		
BH_2	0.3763[b]	10.24		
CH_3	0.3394	9.24	8.92, 8.95	8(*b*)
NH_2	0.3446[c]	9.38[c]		
OH	0.3471	9.44		
F	0.3619	9.85		
Na	0.2671	7.27		
MgH	0.3348	9.11		
AlH_2	0.3606[b]	9.81		
SiH_3	0.3606	9.81		
PH_2	0.3630	9.88		
SH	0.3637	9.90		
Cl	0.3570	9.71	9.24, 9.25	8(*a*), (*c*)
CF_3	0.3951	10.75		
c-Pr	0.3226	8.78		
$HC{\equiv}C$	0.3308	9.00		
$CH_2{=}CH$	0.3101	8.44		
CHO	0.3817	10.39		
CO_2H	0.3839	10.45		
CN	0.3841	10.45	10.07	8(*a*)
NO_2	0.4172	11.35		
Ph	0.2928	7.97	8.06	8(*d*)
NO	0.3897	10.60		
NC	0.3646	9.92		
	0.3379	9.19	8.78	8(*a*)
	0.3103	8.44	8.39	8(*a*)

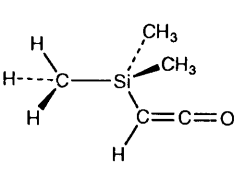
[a] 1 E_h (hartree) $\approx 4.359\,75 \times 10^{-18}$ J. [b] Planar substituent. [c] Pyramidal (planar 0.2877 E_h, 7.83 eV).

Trimethylsilylketene (**5**)

The energies of the monoketene $Me_3SiCH{=}C{=}O$ (**5**) were calculated with the STO-31G and 6-31G** basis sets for the *s-cis* (**5a**) and *s-trans* (**5b**) conformations (Table 2). The *s-cis* conformation was the most stable at both levels of theory. At the highest level examined (HF/31G**//HF/6-31G**, with forced C_s symmetry) it is 3.93 kJ mol^{-1} lower in energy than **5b**. It was also found that the effect on the energy of fixing the C=C=O angle to linearity (179.99°) was very small (0.1 kJ mol^{-1}).



5a



5b

Values of the zero-point energy (ZPE) of **5a** and **5b** were also calculated to ensure that the total energies are good measures of the relative thermodynamic stabilities of silylketene conformations and the values scaled[11] by 0.9 are given

† *Z*-matrices of the optimized geometries of the conformers of 2,3-bis(trimethylsilyl)buta-1,3-diene-1,4-dione (**1a**, **1b** and **1c**), 2,3-bis(di-*tert*-butyldimethylsilyl)buta-1,3-diene-1,4-dione (**4a**, **4b** and **4c**), (trimethylsilyl)ketene (**5a** and **5b**), (*tert*-butyldimethylsilyl)ketene (**6a**, **6b** and **6c**), (*tert*-butyldimethylsilyl)ethene (**7a**, **7b** and **7c**), along with labelled structural formulae, are available as supplementary material (supplementary publication **SUP 57035**, 13 pp.), deposited with the British Library. Details are available from the Editorial office.

Table 2 Calculated total and relative energies of conformers of **5**, **6** and **7**

conformer	total energy/E_h	relative energy /kJ mol^{-1}
5a, *s-cis*[a–c]	−552.312 602	0.00
5b, *s-trans*[a–c]	−552.311 901	1.84
5a, *s-cis*[b–d]	−558.979 237[f]	0.00
5a, *s-cis*[a,b,d]	−558.979 237[f]	0.00[e]
5a, *s-cis*[a,d,f]	−558.979 287	−0.13
5b, *s-trans*[a,b,d]	−558.977 742	3.93[g]
5a, *s-cis*[a,b,h]	−558.974 649	
5b, *s-trans*[a,b,h]	−558.973 050	4.20[i]
6a[b,d,j]	−676.080 264	0.00
6b[b,d,k]	−676.078 292	5.18
6b[d,l]	−676.078 312	5.12
6c[b,d,m]	−676.078 012	5.92
7b, (0.0)[d,n]	−602.372 564	9.98[o]
7, (60.0)[d,n]	−602.372 990	7.86[o]
7, (90.0)[d,n]	−602.375 173	2.12[o]
7a, (115.6)[d,n]	−602.375 981	0.00[o]
7, (140.0[d,n]	−602.372 215	2.01[o]
7c, (180.0)[d,n]	−602.373 513	6.48[o]

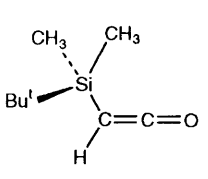
[a] Forced C_s symmetry. [b] C=C=O bond angle fixed at 179.99°. [c] HF/STO-3G//HF/STO-3G. [d] HF/6-31G**//HF/6-31G**. [e] ZPE 375.7 kJ mol^{-1}. [f] C=C=O bond angle optimized (178,62°). [g] ZPE 375.4 kJ mol^{-1}. [h] HF/6-31G**//HF/STO-3G. [i] Relative to *s-cis*. [j] Methyl group *s-cis* to C=C=O. [k] Bu^t group *s-cis* to C=C=O. [l] The C=C=O bond angle was optimized (179.15°). [m] Bu^t group *s-trans* to C=C=O. [n] The dihedral angle between the carbon of the *tert*-butyl group and the plane of the vinyl group. [o] Relative to conformer **7a**. [p] No symmetry (C_s) constraint.

in Table 2. That the ZPE of **5a** is only 0.32 kJ mol^{-1} higher than the ZPE of **5b** shows that it is possible to use uncorrected total energies to study conformational properties of silylketenes. The STO-3G basis set was used in order to ascertain whether the geometries obtained with a minimal basis set are similar to those obtained with the HF/6-31G** basis set and to establish whether the ΔE obtained with HF/6-31G**//HF/STO-3G calculations is comparable to that obtained at the higher level of theory (HF/6-31G**//HF/6-31G**). A good correlation would suggest that the conformational behaviour of large bis(ketenes) such as **1** and **4** can be reliably studied at the HF/6-31G**//HF/STO-3G level of theory. The CH_3—Si bond lengths (1.889 Å) calculated with the 6-31G* basis are 0.024 Å longer than those obtained with the minimal basis set (1.865 Å). The other geometrical parameters (bond lengths, bond angles and dihedral angles) calculated with these basis sets are similar for both conformers. The calculated C—Si bond lengths compare closely to the bond lengths of alkyl- (1.864 ± 0.008 Å) and arylsilanes (1.84 ± 0.01 Å) obtained with X-ray crystallographic structure determinations.[12] These results, coupled with the fact that the ΔE obtained with HF/6-31G**//HF/STO-3G calculations is nearly identical to the ΔE obtained at the HF/6-31G**//HF/6-31G** level of theory, suggest that it is possible to obtain reliable results for large bis(ketenes) at the HF/6-31G**//HF/STO-3G level of theory.

Based on the eigenvectors (orbital coefficients), the HOMO of **5a** is a π-type MO localized predominantly on the C=C bond (C_β, 0.41 and C_α, 0.21) and the oxygen (0.29), but with some mixing with the orbitals of the $(CH_3)_3Si$ group, specifically the out-of-plane methyls (0.11) and the Si (0.08). Because the HF/6-31G** basis set is a split-valence basis set, only the largest coefficients are given. The further orbitals HOMO-1, HOMO-2 and HOMO-3 have substantial σ C—Si character. The LUMO has the largest coefficients on Si (0.30), the C=C bond (C_β, 0.27 and C_α, 0.55), the in-plane methyl (0.39) and the ketene C—H (0.69). It has been suggested based on a frontier molecular orbital analysis that it is the relatively low HOMO–LUMO gap and the size of the orbital coefficients at the oxygen of the HOMO and the carbonyl carbon of the LUMO (or at the methylene carbon of the HOMO and the carbonyl carbon of the LUMO) that determine the rates and regiochemistry of the dimerizations of CH_2=C=O and Me_2C=C=O.[13] However, the calculated HOMO–LUMO gap of Me_3SiCH=C=O (**5**) is 13.53 eV and that of CH_2=C=O is 13.67 eV at the HF/6-31G** level, so the lack of reactivity of the former cannot be ascribed to a large HOMO–LUMO gap.

(tert-*Butyldimethylsilyl*)*ketene* (**6**)

The conformations **6a**–**6c** of (*tert*-butyldimethylsilyl)ketene (**6**) were studied, and the conformer **6a** with a methyl group *cis* to the ketenyl group was found to be the most stable by more than 5 kJ mol^{-1} with the HF/STO-3G and HF/6-31G** basis sets. The total and relative energies obtained with the HF/6-31G** basis set are given in Table 2. Here, as in the case of **5**, fixing the C=C=O bond angle to 179.99° to minimize the cpu requirements has little effect on the energy. At this level of thoery, the Bu^t—Si—C=C dihedral angle of **6a** is 115.37°, and the dihedral angles between the C=C bond and the in-plane and out-of-plane methyl groups are 6.0° and 123.9°, respectively.



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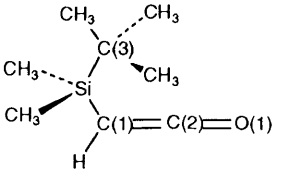

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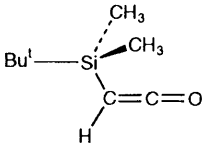


6c

The Bu^t—Si bond lengths of all three conformations are about 0.03–0.04 Å longer than the CH_3—Si bonds, yet these bond lengths (1.920, 1.921 and 1.919 Å) are nearly identical. Thus the Bu^t—Si bond length is considerably longer than the CH_3—Si bond, but there is no significant dependence on the Bu^t—Si—CH=C torsional angle. The orbital energies of the four highest occupied molecular orbitals as a function of the Bu^t—Si—C=C dihedral angle, along with the fitted curves calculated with PESPEC,[2c] are displayed in Fig. 1. As found in the case of Me_3SiCH=C=O (**5**), the HOMO of **6a** is a π-type MO with the largest coefficients being located on the C=C bond (C_β, 0.35 and C_α, 0.19), the oxygen (0.25), the silicon (0.096), the Bu^t carbon (0.14) and the silyl-methyl carbon (0.11) *anti* to the ketene group. The energies of HOMO-1 of **6a**–**6c**, which basically correspond to the Bu^t—Si σ bond, range from 10.6 to 10.8 eV, whereas HOMO-1 of **5a** and **5b**, which correspond to the σ-type MOs of the CH_3—Si, are 11.8 eV, or 1 eV higher. The shift to lower E_i values reflects the normal weaker Bu^t—X bond strength compared with CH_2—X. For the LUMO, the largest coefficients are found on Si (0.26), the C=C bond (C_β, 0.25 and C_α, 0.52), the silylmethyl *anti* to the ketene group (0.73), the silylmethyl *syn* to the ketene group (0.39) and the ketene C—H (0.69).

Conformers with the Bu^t—Si—C=C dihedral angle fixed at 130°, 100° and 60° were also studied with the HF/6-31G** basis set to obtain a potential for twisting about the R_3Si—C bond (plot not shown).

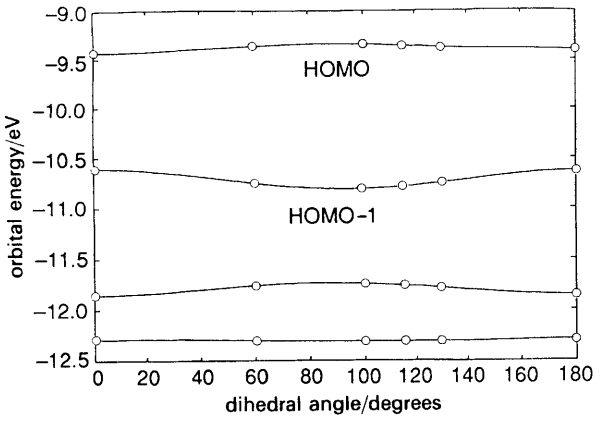


Fig. 1 Angular dependences of the MO orbital energies of the HOMO, HOMO-1, HOMO-2 and HOMO-3 of **6**

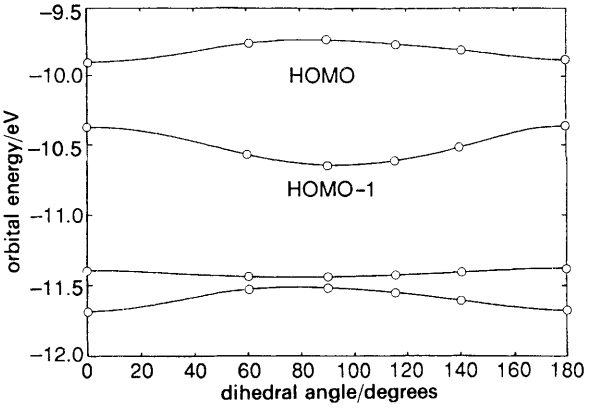
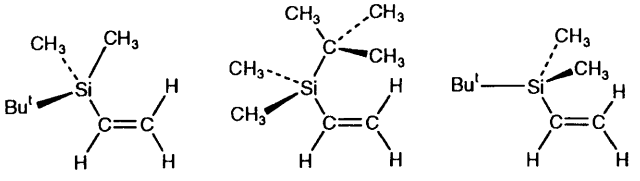


Fig. 2 Angular dependences of the MO orbital energies of the HOMO, HOMO-1, HOMO-2 and HOMO-3 of **7**

(tert-*Butyldimethylsilyl*)*ethene* (**7**)

Six conformers of **7** were studied at the HF/6-31G**//HF/6-31G** level of theory. As found in the case of **6**, the conformer with a methyl group *cis* to the vinyl group is the lowest-energy geometrical structure.



7a **7b** **7c**

The total energies of the six conformers and the energies relative to **7a** are given in Table 2. For **7a** the dihedral angle between the Bu^t group [C(4)] and C(1) of the vinyl group is 115.6°; for the *cis* methyl group, the dihedral angle is 6.15°. These values are virtually identical to the parameters calculated for **6a**. The potential for driving the Bu^t—Si—C=C dihedral angle calculated from the relative energies (plot not shown) with PESPEC resembled that found for **6** except that the ΔE (9.98 kJ mol^{-1}) between **7a** and **7b** was greater than that (5.18 kJ mol^{-1}) between the ketene analogues **6a** and **6b**. This difference is undoubtedly due to the fact that the steric interaction between the Bu^t group and the vinyl group, specifically the vinyl hydrogen at C(1), which is *syn* to the Bu^t group, is greater than the steric interaction between the ketene and Bu^t groups of **6a**. That the calculated C=C—Si bond angle of **7b** is larger (130.8°) than the C=C—Si bond angles of **7c** (124.3°) and **6a** (123.0°) provides support for this proposal. Moreover, the ΔE between **7a** and **7c** is 6.48 kJ mol^{-1}, close to the value (5.92 kJ mol^{-1}) found for **6a** and **6c**. As found in the case of **6**, the HOMO of **7a** is a π-type MO with the largest coefficients being located on the double-bond carbons, the Bu^t quaternary carbon, the carbon of the in-plane methyl and on silicon. HOMO-1 also is a π-type MO with the largest coefficients located on the same atoms as the HOMO. A display of the MO energies of the four highest occupied orbitals as a function of dihedral angle is given in Fig. 2. As in the case of **6**, the fitted curves were calculated with PESPEC. That the HOMO–HOMO-1 gap increases smoothly to 0.91 eV from 0.48 eV when the Bu^t—Si—C=C dihedral angle is decreased to 90° from 180° suggests that there is a very weak σ–π interaction between the Bu^t—Si bond and the π system. As found for **6**, the Bu^t—Si bond of **7** is significantly longer than the CH_3—Si bonds in all the conformations studied by calculation. Even so, the Bu^t—Si bond length of the 90° conformer is virtually identical (1.925 Å) to the Bu^t—Si bond lengths of **6b** (1.924 Å) and **6c** (1.922 Å); the C=C bond lengths (data not given) also show no significant dependence on this dihedral angle. According to the results of the calculations, **6** and **7** exhibit similar conformational properties and orbital interactions, but based on the angular dependence of the HOMO–HOMO-1 gap, the σ–π interaction is greater in the case of **7** than for **6**. Undoubtedly, this is due to the fact that the HOMO–HOMO-1 gap is smaller in **7** than in **6** (see Fig. 1 and 2).

2,3-Bis(trimethylsilyl)buta-1,3-diene-1,4-dione (**1**)

The conformational behaviour of bisketene **1** was studied with semiempirical (AM1)[6] and *ab initio* methods and the relative energies as a function of the C=C—C=C dihedral angles are given in Table 3. The potential obtained from the AM1 energies that were calculated with no symmetry constraints, as displayed in Fig. 3, indicates that conformers with C=C—C=C dihedral angles ranging between 70° and 90° are expected to be the most stable geometrical structures in the gas phase. *Ab initio* calculations were carried out with STO-3G and 6-31G** basis sets with the C=O, C=C, C—Si, C—C and C—H bonds of one-half of **1** set equal to the corresponding bonds of the other R_3Si—CH=C=O fragment, and the C=C=O bond angles fixed at 179.99°. Data obtained with these basis sets (only the 180°, 120°, 105°, 90° and 45° conformers were studied at the 6-31G** level of theory) are given in Table 3. The *ab initio* potentials for twisting about the C(2)C(3) σ bond of the bisketene moiety are displayed in Fig. 3. As found with AM1, twisted conformers are lower in energy than the *s-trans* conformer **1a**, but unlike the results obtained with AM1, at the 6-31G** level the 105°

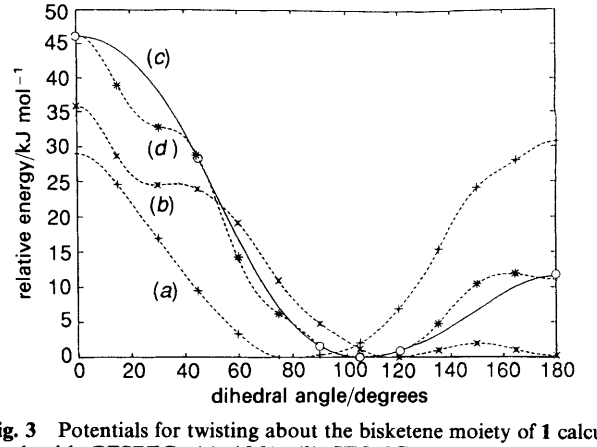


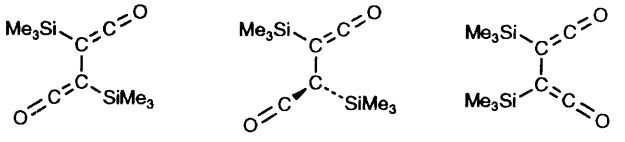
Fig. 3 Potentials for twisting about the bisketene moiety of **1** calculated with PESPEC: (*a*) AM1; (*b*) STO-3G; (*c*) 6-31G**; (*d*) 6-31G**//STO-3G

Table 3 Total and relative energies of conformers **1** and **4**

dihedral angle	Relative energiy/kJ mol^{-1}					
	AM1	STO-3G//STO-3G[b]		6-31G**//STO-3G[b]		6-31G**//6-13G**[b]
	1	**1**	**4**	**1**	**4**	**1**
0	28.97	35.89	56.16	46.26	58.69	46.03
15	24.53	28.62	54.85	38.98	57.77	
30	16.83	24.53	40.35	32.86	39.39	
45	9.24	23.91	28.27	28.70	24.30	28.44
60	3.35	19.15	18.71	14.03	13.86	
75	0.0	10.89	11.80	6.21	7.27	
90	0.33	4.85	7.33	1.78	4.60	1.59
105	1.93	1.13	4.83	0.00[c]	2.82	0.00[d]
120	6.91	0.00[e]	1.30	0.85	0.00[f]	0.87
135	15.20	1.00	0.00[g]	4.82	0.56	
150	24.03	1.90	0.53	10.41	2.99	
165	27.93	1.01	1.80	11.78	5.55	
180	30.69	0.23	2.39	11.07	6.51	11.54

[a] Relative to the calculated $\Delta_f H$ of the 75° conformer (−460.23 kJ mol^{-1}). [b] Relative to the calculated total energy of the lowest-energy conformer. [c] $E = -1116.777\,386\ E_h$. [d] $E = -1116.786\,744\ E_h$. [e] $E = -1103.478\,881\ E_h$. [f] $E = -1350.971\,966\ E_h$. [g] $E = 133.934\,418\ E_h$.

conformer is the lowest-energy geometrical structure; with the STO-3G basis set, the 120° conformer is the lowest-energy geometrical structure. In the case of *s-cis* conformer **1c**, in which the C=C—C=C dihedral angle is fixed at 0°, a steric interaction twists the trimethylsilyl groups out of the π plane by 14.5°.



1a **1b** **1c**

Single-point calculations for **1** were also carried out with the 6-31G** basis set on the STO-3G optimized geometries and the relative energies are also compiled in Table 3. As in the case of **5**, these calculations were carried out to establish whether the potential obtained at the HF/6-31G**//HF/STO-3G level of theory parallels that obtained with the HF/6-31G** basis set geometry. The STO-3G potential (Fig. 3) is flatter, with the *s-trans* conformer similar in energy to the twisted conformers, compared with the HF/6-31G** potential in the region between 180° and 90°, while the HF/6-31G**//HF/STO-3G potential is very similar to that for the HF/6-31G** geometry. These results are in accord with the data obtained for **5** and suggest that calculations at the 6-31G**//STO-3G level can be reliably used to study the conformational properties of bisketenes with substituents on silicon larger than hydrogen, and can be usefully extended to Bu^{t}Me$_2$Si as well.

Because bisketenes **1** (six methyls) and **4** (10 methyls) each have a large number of conformational degrees of freedom, hypersurfaces are required to describe the torsional potentials accurately. Even so, the calculated two-dimensional potentials trace minimum-energy paths through the hypersurfaces. Conformational isomerism about the Si—C bonds also will not affect the HOMO–HOMO-1 splitting or the low-lying E_i levels of the Si—C bonds.

Based on the eigenvectors obtained with the HF/6-31G**//HF/6-31G** calculations, the HOMO of the 105° twisted conformation of the bisketene (**1b**) is basically a π-type MO. The largest coefficients are found on the C=C=O carbons and oxygens; there is a small involvement of Si orbitals. HOMO-1 also has π character involving both ketene groups with a slightly larger involvement of Bu^t—Si orbitals than in the case of the HOMO. The orbitals HOMO-2, HOMO-3, HOMO-4 and HOMO-5 are basically σ-type C—Si orbitals of the Bu^t—Si group. The LUMO is highly delocalized with involvement of the ketene π systems, the silicons and the two in-plane methyl groups. At the 6-31G** level, the HOMO–HOMO-1 splittings calculated for the 180°, 150° and 90° conformers are 3.05, 0.88 and 0.34 eV, respectively. A display of the orbital energies of the four highest molecular orbitals as a function of the O=C=C—C=C=O dihedral angle is given in Fig. 4. The fitted curves were calculated with PESPEC, and this is the reason for the apparent avoided crossing at a torsional angle near 80°. However, it is expected that these curves should cross because the positive combination of the *s-cis* conformer should transform to a negative combination in the *s-trans* conformer, and an estimated crossing is shown with dashed lines.

*2,3-Bis(di-*tert*-butyldimethylsilyl)buta-1,3-diene-1,4-dione* (**4**)

Owing to the size of bisketene **4**, optimized geometries were obtained with the STO-3G basis set as the C=C—C=C dihedral angle was decreased incrementally by 15° starting at 180°. The relative energies of **4** calculated at the HF/STO-3G//HF/STO-3G and HF/6-31G**//HF/STO-3G levels of theory as a function of this dihedral angle are listed in Table 3, and were used to obtain the potentials displayed in Fig. 5. As found in the case of **1**, the STO-3G calculations produced

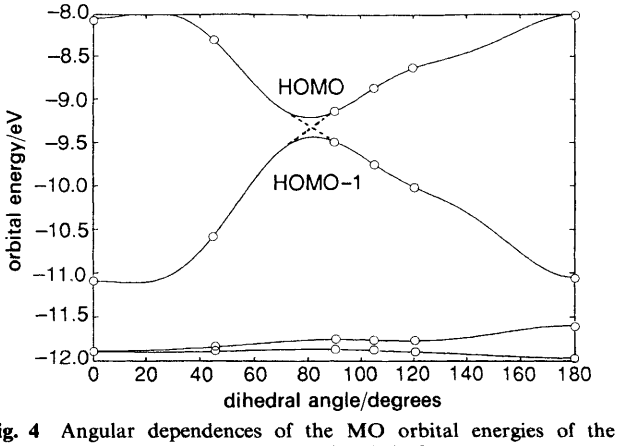


Fig. 4 Angular dependences of the MO orbital energies of the HOMO, HOMO-1, HOMO-2 and HOMO-3 of **1**

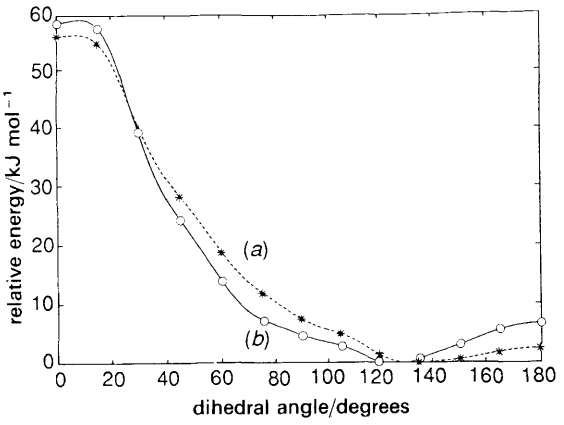
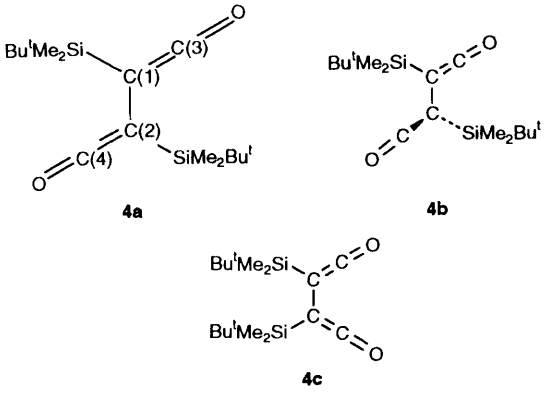


Fig. 5 Potentials for twisting about the bisketene moiety of **4** calculated with PESPEC: (*a*) STO-3G; (*b*) 6-31G**/STO-3G

a potential that is flat in the region between 180 and 90°. However, at the HF/6-31G**//HF/STO-3G level of theory, there is a single minimum in a deeper well and the most stable conformations of **4** have C=C—C=C dihedral angles in the region of 120°. In the case of **1** the most stable conformation has a dihedral angle of 105° at the HF/6-31G**//HF/6-31G** and HF/6-31G**//HF/STO-3G levels of theory. Displays of the eigenvalues of HOMO, HOMO-1, HOMO-2 and HOMO-3 as a function of the dihedral angle are given in Fig. 6. The estimated crossing of the HOMO and HOMO-1 curves is shown as dashed lines.



Photoelectron Spectroscopic Studies and Synthesis of Spectra

The ultraviolet photoelectron spectra of the monoketenes **5** and **6** and the bisketenes **1** and **4** are shown in Fig. 7. The PE spectrum of the alkene **7** is shown in Fig. 8, and selected vertical ionization energies are given in Table 4, together with

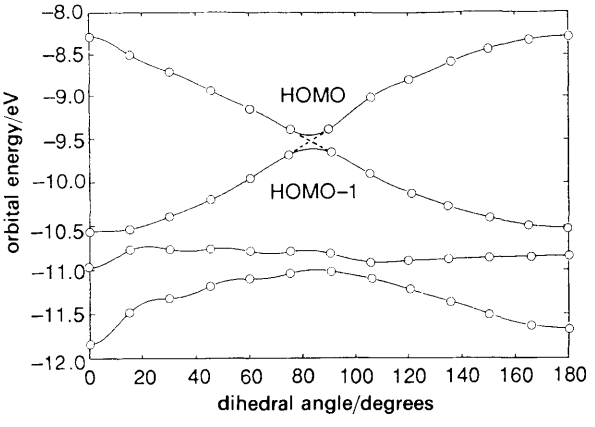


Fig. 6 Angular dependences of the orbital energies of the HOMO, HOMO-1, HOMO-2 and HOMO-3 of **4**

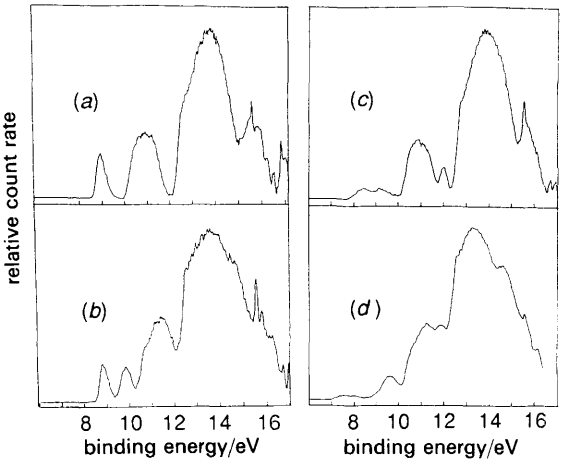


Fig. 7 UV photoelectron spectra: (*a*) **5**, (*b*) **6**, (*c*) **1**, (*d*) **4**

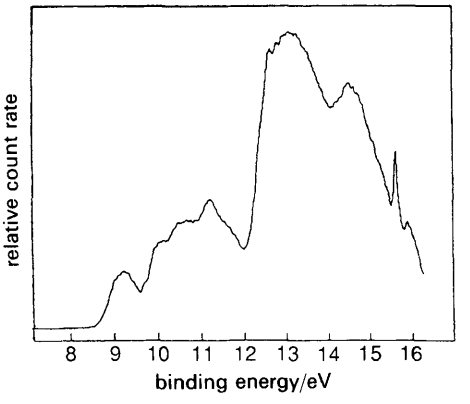


Fig. 8 UV photoelectron spectrum of **7**

the calculated HOMO energies for comparison. The monoketene $Me_3SiCH{=}C{=}O$ (**5**) exhibits a single band centred at 8.95 eV (calculated 9.43 eV) and a group of three overlapping bands centred at 11.0 eV corresponding to the three Si—CH_3 bonds which are resolved from the main group of σ bands [Fig. 7(*a*)]. The relative values of the MO eigenvalues correlate well with the relative E_i values. The general features of the PE spectra of $Bu^tMe_2SiCH{=}C{=}O$ (**6**) and of $Me_3SiCH{=}C{=}O$ (**5**) are the same except that there is a

Table 4 Selected experimental and calculated vertical ionization energies

compound	ionization energy/eV: experimental	ionization energy/eV: calculated (HOMO)	other observed bands
5	8.95[a]	9.43	three bands centred at 11.0 eV
6	8.79[a]	9.36	four or five bands centred at 11.5 eV
	9.85[a]	10.79	
7	9.16[a]	9.77	
	10.1[b]	10.62	
	10.4[b]		
	11.2[b]		
1	8.4[b]	8.87[c]	four or five bands centred at 12.0 eV
	9.1[b]	9.75[c]	
4	7.7[b]	8.80[d]	two bands centred at 9.7 eV
	9.6[e]	10.11[d]	

[a] Estimated error: ±0.025 eV. [b] Estimated error: ±0.05 eV. [c] 105° conformer. [d] 120° conformer. [e] Estimated from the shoulder on the band centred at 9.7 eV.

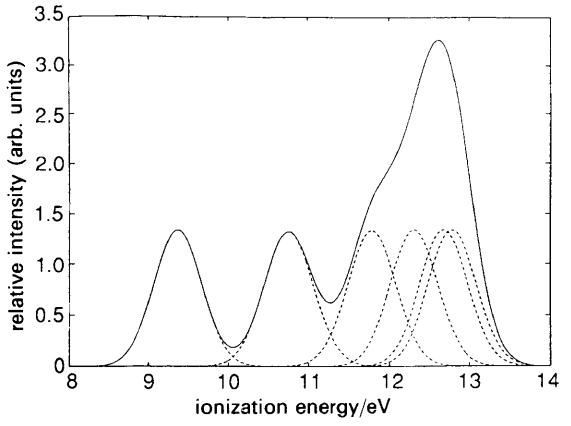


Fig. 9 Display of the synthetic partial UV photoelectron spectrum of **6** calculated with PESPEC

second low E_i band at 9.85 eV (calculated 10.79 eV) for the former corresponding to the Bu^t—Si bond, as predicted by these calculations. The MO eigenvalues correlate remarkably well with the relative values of the vertical E_is. For **1** and **4**–**7** the absolute values of the eigenvalues of the highest occupied MOs are, on average, 0.61 eV higher (Fig. 1 and 2) than the E_i values (Table 4). This is consistent with the results for the other monoketenes (Table 1) for the same reasons. The synthetic spectrum of **6** obtained with PESPEC and the potential given in Fig. 1 is displayed in Fig. 9. Only the eigenvalues of six MOs (HOMO to HOMO-5) were used to synthesize the partial spectrum that was convoluted with a Gaussian lineshape with a full width at half height (FWHH) of 0.7; the temperature was set at 300 K. In the case of **7** the lowest E_i (9.15 eV) is less than the E_i values of $SiH_3CH{=}CH_2$ (10.37)[4a] and $MeSiH_2CH{=}CH_2$ (9.86)[4b] in keeping with the increase in the number of alkyl groups on silicon. That the partial synthetic spectrum of **6** accurately reproduces the low E_i regions of the PE spectrum validates the application of a combination of *ab initio* calculations and PE spectroscopy to the study of the conformational behaviour of bisketenes **1** and **4**. The PE spectrum of **1** as displayed in Fig. 7(*c*), shows two broad overlapping bands at 8.4 and 9.1 eV ($\Delta E_i = 0.7$ eV), in addition to the broad feature due to four or five bands centred at 11 eV and the relatively sharp band at 12.0 eV, both resolved from the main sigma envelope. The partial spectrum of **1** calculated from the HF/6-31G**//HF/6-31G** potential (see Fig. 3) and the eigenvalues of the eight highest occupied molecular orbitals from PESPEC is displayed in Fig. 10. A Gaussian convolution of 0.7 and a temperature of 300 K were used in the calculations. The synthetic spectrum

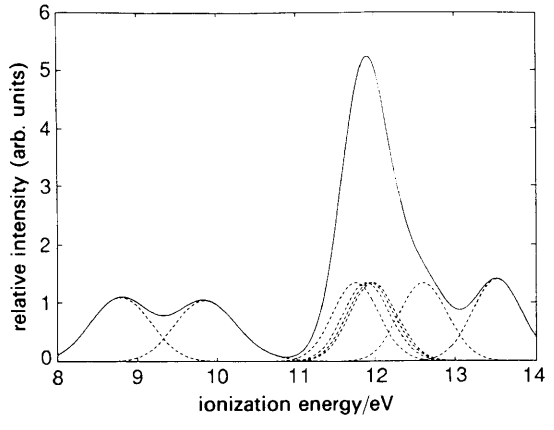


Fig. 10 Display of the synthetic partial ultraviolet photoelectron spectra of **1**

accurately reproduces the broad overlapping low-E_i bands, the HOMO–HOMO-1 splitting of less than 1 eV, and the portion of the higher E_i band structure of the PE spectrum. Just as for the monoketenes **5** and **6** the calculated values are *ca.* 0.5 eV higher in energy than those observed in the gas phase.

The PE spectrum of the bisketene **4** is displayed in Fig. 7(*d*), and only one broad band centred at 7.7 eV is completely resolved from the main group of overlapping bands. That the E_i of this band is lower than the low E_i band of **1** is consistent with the expectation of a larger HOMO–HOMO-1 splitting for **4** compared with the splitting of **1**. This is a consequence of the fact that conformers with larger C=C—C=C dihedral angles (120°) should be preferentially populated for **4** (Fig. 5) compared with **1** (105°). From the shoulder on the next series of overlapping bands, we estimate that the next band has a maximum at *ca.* 9.6 eV yielding a HOMO–HOMO-1 splitting of 1.9 eV. This result is in accord with the splitting obtained from the partial synthetic spectrum of **4** (not shown) which shows that the larger HOMO–HOMO-1 splitting causes the HOMO-1 band to overlap the low-E_i bands arising from the σ-type C—Si molecular orbitals of the Bu^t—Si groups, a result that correlates with the PE spectrum. The experimental and synthetic spectra provide strong evidence that **4** also prefers twisted conformations in the gas phase, but with C=C—C=C dihedral angles that are larger than in the case of **1**.

An alternative explanation, suggested by a referee, is that the 7.7 eV band consists of both the negative and positive combinations of the ketenyl π_{CCO} orbitals, and that the 9.6 eV band of **4** correlates with the 9.85 eV band of **6**, and arises from the Bu^t—Si bond. This would require the C=C—C=C dihedral angle to be closer to 90° than our assignment of 120°.

Dipole Moments

Dipole moments have frequently been used for the determination of conformations in α,β-unsaturated systems,[14a] and as an independent experimental test of the preferred conformation of the bisketene **1**, dipole moments of **1** and the monoketene $Me_3SiCH{=}C{=}O$ (**5**) were determined [14b,c] in cyclohexane as 2.7 ± 0.3 and 1.8 ± 0.3 D,† respectively. This large measured dipole moment of the bisketene rules out the *anti*-planar conformation **3a**, which would have a zero dipole moment, but is consistent with a variety of other geometries ranging from near perpendicular to *syn*-coplanar. The measured value of 2.7 D corresponds to a calculated dihedral angle of 80° between the dipoles of two monoketenes, but values of 0° to 120° fall within the uncertainty of the measurements. The HF/6-31G**//HF/6-31G** *ab initio* calculated dipole moments of **5** and the 105° conformer of **1** are 1.86 and 2.33 D, respectively, and agree well with the experimental values.

Conclusions

We have shown for the monoketenes that the calculated HOMO energies and the ionization energies correlate well with available experimental values and may be understood in terms of the effects of these substituents on the ketenes. The calculated orbital energies and experimental ionization energies of the Bu^{t}Me$_2$Si substituted ketene **6** and alkene **7** show a lowering by 1 eV relative to the Me$_3$Si analogues of the HOMO-1 level, ascribed to weakening of the Si—C bond for the Bu^t group. The conformations of the bisketenes

† 1 D (Debye) $\approx 3.335\,64 \times 10^{-30}$ C m.

$(RC{=}C{=}O)_2$ are calculated to be twisted out of linearity by 105° for R = Me_3Si and 120° for R = Bu^tMe_3Si, and the experimental spectra are in agreement with this conclusion. The dipole moment of **1** rules out an *anti*-periplanar conformation, and is consistent with a twisted conformation.

Experimental

Monoketenes **5**[15a] and **6**[15b] and bisketenes **1**[1a,b] and **4**[1b] were obtained as has been described. To prepare **7** a solution in THF–diethyl ether–pentane of $CH_2{=}CHLi$ prepared as described[15c] from $CH_2{=}CHBr$ (2.3 g, 31.5 mmol) in a 50 ml round-bottom flask at −78 °C was added dropwise to a solution of *tert*-butyldimethylsilyl chloride (4.1 g, 27.2 mmol, Aldrich) under N_2 at −78 °C. The mixture was kept at room temperature for four days, and ^1H NMR analysis showed the reactant : product ratio to be 59 : 41, indicating 52% conversion. The reaction mixture was washed with H_2O, dried over $MgSO_4$ and fractionally distilled. The fraction with bp 65–75 °C contained THF and the desired product **7**, and the latter was collected by preparative VPC (3 m × 1 cm OV-17 column, 40 °C) to give **7** as a colourless oil: ^1H NMR, δ ($CDCl_3$) 0.027 (s, 6), 0.87 (s, 9), 5.67 (dd, 1, *J* 4.9, 19.5 Hz), 6.00 (dd, 1, *J* 4.9, 14.7 Hz), 6.15 (dd, 1, *J* 19.5, 14.7 Hz); ^{13}C NMR, δ ($CDCl_3$) −6.51, 16.28, 26.33, 132.27, 137.40; IR, $\nu_{max}(CDCl_3)/cm^{-1}$: 1592 (C=C); EIMS *m/z* 142 (M^+, 4), 85 (M^+-Bu^t, 100), 73 (22), 59 (54); HRMS *m/z*, calculated for $C_8H_{18}Si$ 142.1178, found 142.1175.

PE spectra were measured with a locally constructed instrument[16] by signal averaging 20–30 scans with argon as the calibrant. To ensure that the scale was linear over the 10 eV range, a variable offset was used at the beginning of the scans and calibrations were also run with acetone (E_i = 9.70 eV) and O_2 (E_i = 12.30 eV).

Dipole moments were obtained with a Dekameter DK03 instrument (Wissenschaftlich-Technische, Werkstratten GmbH) and an Abbe refractometer by a reported method[14b] and calculated procedure.[14c] A series of cyclohexane solutions of bisketene **1** and monoketene **5** were utilized to give dipole moments of 1.8 D for **1** and 2.7 D for **5**.

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