Preparation and crystal structure of a stable and persistent twisted tetraketene

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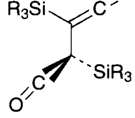
Thermolysis of bis(cyclobutenedione) 8 leads to the tetraketene 7, whose X-ray structure confirms the twisted arrangement of the adjacent ketenyl groups predicted by theory.

Bisketenes have been the recent object of attention in our laboratory,[1,2] including not only studies of 1,2-bisketenes **1**,[1] but also carbon suboxide **2**,[3a] a 1,1-bisketene, and the first 1,3-bisketene, **3**.[3b] We have also prepared and studied the first trisketene **4**,[3b] which is stable and persistent, and a tetraketene **5**, which is relatively long-lived but which at elevated temperatures reverts to the more stable bis(cyclobutenedione) **6**.[3d] Now these studies have been extended to the tetraketene **7**.

The desired precursor for **7** is the bis(cyclobutenedione) **8** and the strategy for the preparation is shown in eqns. (1–3). Reaction of **9** with lithium trimethylsilylacetylide gave the bisalkyne **10**,† which reacted with dichloroketene generated using zinc dust in 1,2-dimethoxyethane (DME), activated by heating[4a] and sonication,[4b] to give **11**. Three regioisomers of **11** are expected and 1,3-chloride migration in **11** could lead to other isomers. Upon hydrolysis all three regioisomers of **11** are expected to give **8**. The ^{1}H NMR spectrum of the crude solid product **11**, formed in approximately 90% yield, showed several products. After chromatography and recrystallization, one was isolated pure, and was tentatively identified as **11a** based on its spectral properties.† Hydrolysis of the mixed product gave **8**.†

Heating pure **8** in a sealed ampoule under argon at 115 °C for 1 h gave **7**† as a solid product which was dissolved in pentane, and upon slow evaporation of the pentane under a stream of argon at −78 °C gave a large yellow–orange crystal suitable for X-ray analysis, as illustrated in Fig. 1.‡,[5] The derived bond distances and bond angles have rather small uncertainties, as reported in Table 1, agree well with dimensions calculated for the bisketenes **1a** (R = Me)[2c] and **1b** (R = H).[2a]

Of particular note is the observed 119° dihedral angle between each pair of adjacent ketenyl groups. The non-coplanarity of the two ketenyl groups of 1,2-bisketenes was predicted by us[2a,c] on the basis of *ab initio* calculations and has been supported in the case of **1a** by the measured dipole moment and photoelectron spectrum.[2c] This preference for a twisted conformation is not primarily due to steric effects, as even the parent 1,2-bisketene $(\mathrm{CH{=}C{=}O})_2$ is calculated to prefer a non-planar conformation by 10.0 kJ mol^{-1} compared to the *anti*-conformation.[1b,2a]



1a R = Me
b R = H

O=C=C=C=O

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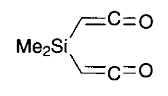

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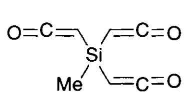

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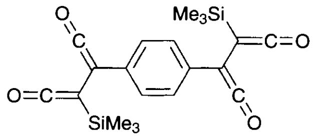

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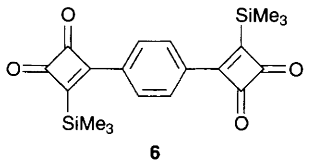

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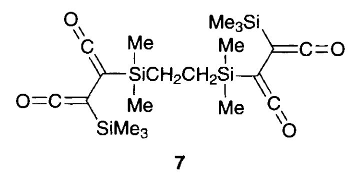
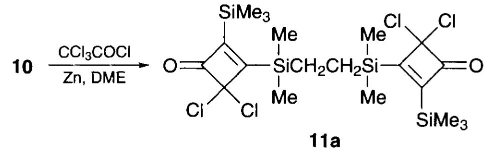


7

$$\underset{\mathbf{9}}{\mathrm{ClMe_2SiCH_2CH_2SiMe_2Cl}}$$

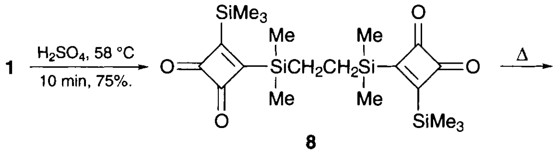
$$93\%\ \Big\downarrow\ \mathrm{Me_3SiC{\equiv}CLi}$$

$$\underset{\mathbf{10}}{\mathrm{Me_3SiC{\equiv}CSiMe_2CH_2CH_2SiMe_2C{\equiv}CSiMe_3}} \qquad (1)$$



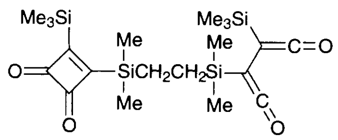
11a

(2)



8

(3)



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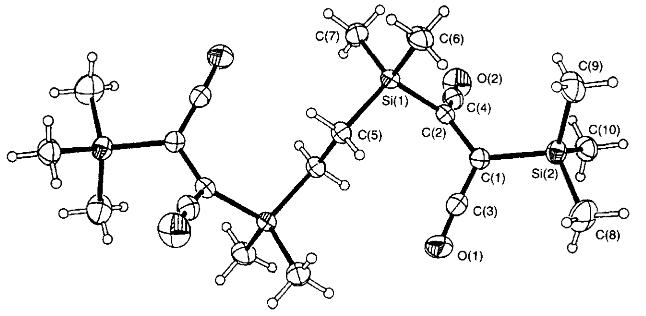

Fig. 1 X-Ray crystal structure of tetraketene **7**

Table 1 Selected observed bond distances (Å) and bond angles (°) for **7**, and comparative calculated values for **1**

Bond lengths				
7	C(1)–C(3)	C(1)–C(2)	C(3)–O(1)	C(1)–Si(2)
	1.305(2)	1.507(2)	1.163(2)	1.8771(13)
	C(2)–C(4)		C(4)–O(2)	C(2)–Si(1)
	1.307(2)		1.169(2)	1.8788(12)
1[a]	1.312	1.518	1.145	1.890
1[b]	1.315	1.514	1.141	1.869
Bond angles				
	C(3)–C(1)–C(2)	C(3)–C(1)–Si(2)	C(2)–C(1)–Si(2)	C(1)–C(3)–O(1)
	120.42(12)	116.34(10)	123.16(9)	176.6(2)
	C(4)–C(2)–C(1)	C(4)–C(2)–Si(1)	C(1)–C(2)–Si(1)	C(2)–C(4)–O(2)
	121.41(11)	116.60(10)	121.97(8)	175.5(2)
1[a]	117.6	117.9	124.5	179.99[c]
1[b]	118.2	119.3	122.5	178.7
Torsion angles				
7	C(3)–C(1)–C(2)–C(4)	Si(2)–C(1)–C(2)–Si(1)		
	118.95(16)	113.82(9)		
1[a]	105.0[c]	107.7		
1[b]	92.0	89.5		

[a] Ref. 2(*c*) HF/6-31G**. [b] Ref. 2(*a*), HF/6-31G*. [c] Fixed.

Table 2 Rate constants for ring opening of **8** to **7** in isooctane

T/°C	10^5k_1/s^{-1}[a]	10^5k_2/s^{-1}[b]
83.5	21.6 ± 0.8	23.4 ± 0.4
74.0	6.15 ± 0.03	7.49 ± 0.03
69.5	2.72 ± 0.04	3.81 ± 0.02

[a] $\Delta H^\ddagger$ = 145 kJ mol^{-1}, $\Delta S^\ddagger$ = 90.0 J K^{-1} mol^{-1}. [b] $\Delta H^\ddagger$ = 128 kJ mol^{-1}, $\Delta S^\ddagger$ = 41.8 J K^{-1} mol^{-1}.

The kinetics of formation of **7** from **8** were monitored by the decrease in the UV absorption at 221.5 nm upon heating **8** in isooctane. The data were best fitted as showing two consecutive first-order rate processes, as shown in Table 2. For comparison the rate interpolated for the ring opening of the corresponding cyclobutenedione to form **1a** at 74.0 °C is 5.75 × 10^{-5} s^{-1} ($\Delta H\ddagger$ = 117 kJ mol^{-1}, $\Delta S\ddagger$ = 13 J K^{-1} mol^{-1}),[1c,e] which is essentially the same as k_1 for **8** (Table 2).

A solution of pure **8** in CDCl$_3$ was purged with argon and heated at 100 °C, and the ^{1}H NMR spectrum was observed at intervals. The only product observed at the completion of the reaction was the tetraketene **7**, as indicated by the ^{1}H NMR signals at δ 0.182 (SiMe$_2$), 0.204 (SiMe$_3$) and 0.587 (CH$_2$), and the ^{29}Si NMR signals at δ 3.40 and 6.82, in agreement with data for other ketenes,[1d] but at intermediate times signals assigned to the Me$_3$Si protons of bisketene **12** were observed at δ 0.19 and 0.36. Integration of the ^{1}H NMR signals of the CH$_2$ groups of **7** and **8** after 10 and 25 min permitted the calculation of rate constants of 1.1 ± 0.6 × 10^{-3} and 1.6 ± 0.6 × 10^{-3} s^{-1} for the disappearance of **8** and for the formation of **7**, respectively, corresponding to the first and second ring opening, respectively, in good agreement with the values of 2.00 × 10^{-3} and 1.68 × 10^{-3} s^{-1}, respectively, extrapolated from the rates obtained by UV.

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Footnotes

† *Selected data* for **10**: mp 44–47 °C; δ_H (CDCl$_3$) 0.144 (s, 12, SiMe$_2$), 0.169 (s, 18, SiMe$_3$), 0.580 (s, 4, CH$_2$); δ_C −2.31, −0.15, 8.34, 113.02, 114.40; δ_{Si}(CDCl$_3$) −18.88, −14.86. For **11a**: mp 109–110 °C; ν_{max}(CDCl$_3$)/cm^{-1} 1774; δ_H(CDCl$_3$) 0.268 (s, 18, SiMe$_3$), 0.422 (s, 12, SiMe$_2$), 0.871 (s, 4, CH$_2$); δ_C(CDCl$_3$) −3.04, −1.18, 7.66, 96.78, 169.58, 183.71, 195.00; δ_{Si}(CDCl$_3$) −10.46, −3.60. The tentative assignment of the stereochemistry is based on the NMR equivalence of the pairs of groups in the molecule, the assignment of the SiMe$_3$ and SiMe$_2$ ^{13}C signals based on the ^{13}C, ^{1}H coupled spectra and the upfield shift of the resonance of the Me on Si β to the carbonyl groups. For **8**: mp 93–95 °C; ν_{max}(CDCl$_3$)/cm^{-1} 1769; δ_H(CDCl$_3$) 0.356 (s, 30, SiMe$_3$ and SiMe$_2$), 0.770 (s, 4, CH$_2$); δ_C(CDCl$_3$) −3.61, −1.47, 6.83, 201.52, 201.77, 215.82, 217.78; δ_{Si}(CDCl$_3$) −8.29, −5.15; λ_{max} (hexane)/nm 221.5 (ε 26,000), 352 (92). For **7**: mp 25–27 °C; ν_{max}(CDCl$_3$)/cm^{-1} 2084; δ_H(CDCl$_3$) 0.182 (s, 12, SiMe$_2$), 0.204 (s, 18, SiMe$_3$), 0.587 (s, 4, CH$_2$); δ_C(CDCl$_3$) −3.29, −0.85, 4.43, 5.62, 7.71, 181.39, 181.70; δ_{Si}(CDCl$_3$) 3.40, 6.82.

‡ *Crystal Data* for **7**: C$_{20}$H$_{34}$O$_4$Si$_4$, M_r = 450.83, triclinic space group $P\bar{1}$, a = 8.4163(9), b = 9.6697(13), c = 9.7922(11) Å, α = 63.945(9), β = 71.617(9), γ = 74.245(9)°, U = 671.08(14) Å^3, Z = 1, D_c = 1.116 g cm^{-1}, μ = 2.42 cm^{-1}, T = 173(2) K, Mo-Kα radiation (λ = 0.71073 Å), graphite monochromator, Siemens P4 diffractometer, $2\theta_{max}$ = 60°, ω scans, 3804 independent reflections, R_{int} = 0.0179, no absorption correction, structure solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL/PC. All non-hydrogen atoms were refined with anisotropic displacement parameters and the hydrogen atoms were refined isotropically. 195 Refined parameters gave, $R1$ = 0.0349, $wR2$ = 0.0894 for 2987 reflections with $I > 2\sigma(I)$ and $R1$ = 0.0466, w$R2$ = 0.0937 for all data, minimum and maximum features in final difference map were −0.181 and 0.415 e Å^{-3}.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/194.

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