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THE STRUCTURE OF SILYLCYCLOHEPTATRIENES

CHRISTOPHER GLIDEWELL

Chemistry Department, University of St. Andrews, St. Andrews, Fife KY16 9ST (Great Britain)

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Summary

Calculations have been made, using the MNDO method, of the structures and energies of four isomeric forms of η^1-$SiH_3C_7H_7$ and of η^7-$SiH_3C_7H_7$. The transition state has been identified for the [1,5] shift of the SiH_3 group in η^1-$SiH_3C_7H_7$, but no transition state could be located for any other SiH_3 migration pathway: this is consistent with orbital-symmetry control of the rearrangement. Conformational preferences in 7-substituted cycloheptatrienes and 1-substituted cyclohexanes are briefly compared.

Introduction

In a recent paper [1] we reported the results of MNDO calculations of the structures and energies of some isomeric silylcyclopentadienes. The results of the calculations were in general in very reasonable accord with experimental findings: the geometry calculated for the 5-isomer of $SiH_3C_5H_5$ was in satisfactory agreement with that found by electron diffraction [2]; the 1- and 2-isomers of both $SiH_3C_5H_5$ and $Me_3SiC_5H_5$, formed by prototropic shifts were calculated to have lower $\Delta H_f^{\ominus}$ values than the corresponding 5-isomers, consistent with the rearrangements observed experimentally [3,4,5]; and the migration pathway of the SiH_3 group in the $SiH_3C_5H_5$ rearrangement was found to be a [1,2] shift ($\equiv$ [1,5]) rather than a [1,3] shift, again in accord with experimental observations [3].

Fortified by the reasonably good reproduction by MNDO of experimental data in the silylcyclopentadiene series, we have now turned our attention to the silylcycloheptatrienes. Here there are several additional features which make these a more complex, and hence more interesting, series than the cyclopentadienes.

Firstly, whereas unsubstituted cyclopentadiene is planar [6] with C_{2v} symmetry, so that the two sites in the CH_2 group are identical, the unsubstituted cycloheptatriene has a non-planar tub-shaped C_7 skeleton of only C_s symmetry [7]. Consequently the sites in the CH_2 are now non-equivalent, such that one is approximately axial and the other approximately equatorial. Conformational isomerism is possible, and

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although the barrier for ring inversion is small, ca. 25 kJ mol^{-1} in cycloheptatriene itself [8], the presence of 1-substituents raises this barrier markedly, allowing the possibility of conformationally stable isomers. In the triphenyltin derivative $Ph_3SnC_7H_7$, the substituent was found [9] by X-ray analysis to occupy the quasi-axial site.

Secondly, the least-motion and orbital-symmetry predictions for migration of a substituent no longer lead to the same migration, as is the case in a substituted cyclopentadiene. In both series, a suprafacial sigmatropic shift is predicted [10,11] by the Woodward–Hoffman rules to be of type [1,5]. For the cyclopentadiene case a [1,5] shift is equivalent to a [1,2] shift so that least-motion and orbital-symmetry predictions coincide: for the cycloheptatriene case, the least-motion principle predicts [1,2] ≡ [1,7] shifts while orbital-symmetry predicts [1,5] ≡ [1,4] shifts. For a single example only, $Ph_3SnC_7H_7$ have these predictions been tested experimentally [12,13] and in this case the observations clearly support the orbital-symmetry model. However in the next member of the series, $R_3SnC_9H_9$, the experimental data support a least-motion pathway for substituent migration, rather than the pathway predicted by orbital-symmetry considerations [14].

Silicon-, germanium-, and tin-substituted 7-cycloheptatrienes all undergo prototropic shifts to yield non-fluxional isomers [15], whose properties have not been extensively investigated. In the present paper, we report upon MNDO calculations on the equilibrium structures and energies, of a number of silylcycloheptatriene isomers, $SiH_3C_7H_7$, and of the transition states for silyl migrations, which in turn allows a distinction to be drawn between the orbital-symmetry and least-motion pathways: finally a brief comparison is made of conformational preferences in mono-substituted 7-cycloheptatrienes and cyclohexanes.

Method

All calculations were made using the MNDO method [16,17], with the published parameterization for silicon [18], implemented on a VAX 11/780 computer. Equilibrium structures of all η^1 isomers were optimised without any geometrical assumptions. For the η^7 isomers of $SiH_3C_7H_7$, local C_{7v} symmetry was imposed on the cycloheptatrienyl ring: the rotational barrier between the two symmetric tops in this isomer proved to be negligible, so that such an isomer is properly regarded as non-rigid, in a point group of order 42. For all transition state calculations, C_s symmetry was imposed.

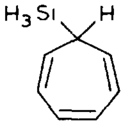
Results and discussion

Equilibrium structures

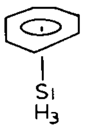
The synthesis of Group IV-cycloheptatrienyl derivatives, by reaction of an triorgano anion of a Group IV element R_3M^- (M = Si, Ge, Sn, Pb) either with C_7H_7X, where X represents a good leaving group, or with the tropylium cation, $C_7H_7{}^+$ [15] will necessarily give rise initially to a product in which there is one hydrogen per carbon atom in the cycloheptatriene ring. Several initial isomers are plausible in which the ring may be bonded to M in η^1, η^3, η^5 or η^7 modes: in these bonding modes the ring could be acting respectively as a 1, 3, 5 or 7 electron ligand towards M. Experimentally, when M = Si, Ge or Sn, the products $Ph_3MC_7H_7$ are

η^1-derivatives [9,15], with no hint, even for M = Sn of any tendency even towards the η^3 mode [9].

Consistent with this, the present MNDO calculations indicate that the η^1-isomer (I) is of much lower energy than the η^7-isomer (II) (Table 1).



(I)



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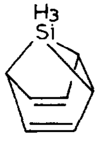
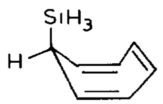


(III)

The η^7-isomer does not represent a minimum on the potential energy surface, but rather a saddle-point: no η^5-isomer could be located at all on the surface, although an η^3-isomer (III) was found, but not otherwise investigated, having $\Delta H_f^\ominus$ of around 420 kJ mol^{-1}.

The detailed geometries calculated for the parent hydrocarbon C_7H_8 and for 7-$SiH_3C_7H_7$ are given in Table 2 together with the experimental geometries found in the gas-phase for C_7H_8 [7] and in the crystalline state for 7-$Ph_3SnC_7H_7$ [9]. In terms of bond lengths, the agreement between the observed and calculated values is good: the agreement for the bond angles is less good as the sums of the angles within the ring are calculated to be too large (i.e. the ring is calculated to be insufficiently puckered). The angle sum calculated for C_7H_8 is 896°, compared with 851° found experimentally [7], while for 7-$SiH_3C_7H_7$ the calculated sum is 898° in the aquatorial conformer and 894° in the axial, to be compared with 862° found in 7-$Ph_3SnC_7H_7$ [9]. Associated with this point in the under-estimate of the ring dihedral angles α and β (defined in Table 2) which again shows the ring to be calculated much too near to planarity.

7-$SiH_3C_7H_7$ is calculated to exist in two conformers, having the SiH_3 group axial (IV) and equatorial (V) respectively. With the exception of the ring dihedral angles α



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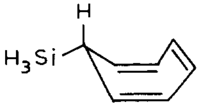


(V)

TABLE 1

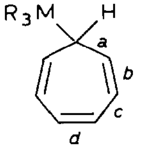
CALCULATED MOLECULAR ENERGIES

Molecule	$\Delta H_f^\ominus$ (kJ mol^{-1})
C_7H_8	+143.1 [a]
7-$SiH_3C_7H_7$ (axial)	+121.8
7-$SiH_3C_7H_7$ (equatorial)	+129.7
1-$SiH_3C_7H_7$	+115.8
2-$SiH_3C_7H_7$	+111.0
3-$SiH_3C_7H_7$	+112.5
η^7-$SiH_3C_7H_7$	+451.1

[a] Experimental $\Delta H_f^\ominus$, +182.8 kJ mol^{-1}, ref. 19.

TABLE 2

CALCULATED AND OBSERVED GEOMETRIES FOR CYCLOHEPTATRIENES

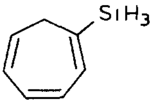


	C_7H_8 (obs) [a]	C_7H_8 (calc)	$7\text{-}SiH_3C_7H_7$ (axial)	$7\text{-}SiH_3C_7H_7$ (equatorial)	$7\text{-}Ph_3SnC_7H_7$ [c]
Distances (Å)					
a	1.505	1.501	1.494	1.495	1.48
b	1.356 [b]	1.350	1.351	1.350	1.32
c	1.446	1.455	1.459	1.456	1.41
d	1.356 [b]	1.355	1.352	1.354	1.32
C–M	–	–	1.865	1.865	3.07
Bond orders					
a	–	0.982	0.988	0.987	–
b	–	1.871	1.864	1.865	–
c	–	1.041	1.037	1.040	–
d	–	1.822	1.827	1.823	–
C–M	–	–	0.867	0.879	–
Angles (°)					
aa′	113.1	119.9	118.8	120.0	114
ab	121.8	130.6	130.5	131.5	123
bc	127.2	129.3	129.1	129.8	125
cd	119.8	128.2	127.8	128.1	126
Dihedral angles [d] *(°)*					
α	41	15.2	19.7	9.9	46
β	37	8.9	10.5	3.4	29

[a] Ref. 7. [b] Mean value of *d*(C=C), ref. 7. [c] Ref. 9. [d] Dihedral angle α between normals to planes defined by *aa′* and by *bb′*; dihedral angle β between normals to planes defined by *bb′* and by *cdc′*.

and β, the geometrical parameters for these two conformers are rather similar (Table 2), but the axial conformer is the more stable by ca. 8 kJ mol^{-1}. We shall return to the question of conformational preference below.

Compounds $7\text{-}R_3MC_7H_7$ undergo rearrangement via hydrogen migration to yield other isomers [15]: for $7\text{-}SiH_3C_7H_7$ the three possible rearrangement products, VI, VII and VIII, are all calculated to be of lower energy than the 7-isomer (I), Table 1.



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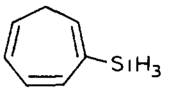

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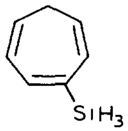


(VIII)

As for the 7-isomer, VI, VII and VIII all contain non-planar C_7 rings, but these no longer have C_s symmetry, so that the definition of ring conformation is no longer straightforward.

The geometry of $\eta^7\text{-}SiH_3C_7H_7$ is summarised in Table 3, along with the appropriate parameters for the isolated $C_7H_7{}^+$ cation: particularly noteworthy is the

TABLE 3

CALCULATED GEOMETRIES OF η^7-$SiH_3C_7H_7$ AND $C_7H_7^+$

	η^7-$SiH_3C_7H_7$	$C_7H_7^+$
d(C–C) (Å)	1.405	1.406
p(C–C)	1.371	1.378
d(C–Si) (Å)	2.892	–
p(C–C)	0.026	–
d(Si–X) (Å) [a]	2.396	–

[a] X represents the centre of the C_7 ring.

long distance from silicon to the ring centre. This, together with the net charges (see below) indicate that this molecule ought perhaps to be best regarded as an ion pair SiH_3^-, $C_7H_7^+$: however the calculated value of $\Delta H_f^{\ominus}$, +451.1 kJ mol^{-1} is considerably less than the calculated $\Delta H_f^{\ominus}$ value for ($SiH_3^- + C_7H_7^+$), +816.2 kJ mol^{-1}.

Electronic structures

Although in the puckered-ring conformation of C_7H_8, a rigorous distinction between σ and π is not possible, nevertheless the modest extent of the puckering calculated still allows identification of the three occupied quasi-π orbitals of the C_7 skeleton. These have calculated binding energies of 8.61, 10.41, and 11.62 eV respectively, and the first of these may be compared, assuming Koopmans' theorem, with the observed ionisation potential, 8.5 eV [20,21]. The total bond orders calculated are given in Table 2.

In the axial isomer of η^1-$SiH_3C_7H_7$, the binding energies of the quasi-π orbitals of the ring are 8.47, 10.39 and 11.25 eV: the bond orders in the rings differ scarcely at all from those in the parent C_7H_8. The Si–C distances, 1.865 Å (×1); 2.743 Å (x2); 3.696 Å (x2); and 4.267 Å (x2), and the corresponding bond orders, 0.867, 0.008, 0.016, and 0.002, respectively, confirm the mono-hapto nature of the silicon-ring binding.

Table 4 lists the calculated net charges on the SiH_3 group and the C_7H_7 ring, and the dipole moments, for all the isomers of $SiH_3C_7H_7$: for each of the mono-hapto isomers the SiH_3 group acts as an electron donor, slightly more effectively when bound to a 3-coordinate carbon than when bound to a 4-coordinate carbon, consistent with the greater electronegativity of the former type which has more s-orbital character in its bond to silicon. On the other hand, the hepta-hapto isomer

TABLE 4

CALCULATED NET CHARGES IN ISOMERS OF $SiH_3C_7H_7$

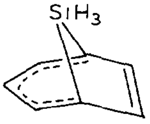
Isomer	$q(SiH_3)$ (e)	$q(C_7H_7)$ (e)	q(C-Si) [a] (e)	μ (D) [b]
7-axial	+0.142	−0.142	−0.122	0.29
7-equatorial	+0.143	−0.143	−0.125	0.30
1-	+0.187	−0.187	−0.307	0.50
2-	+0.204	−0.204	−0.275	0.46
3-	+0.206	−0.206	−0.274	0.60
η^7-	−0.911	+0.911	+0.058	9.91

[a] Charge on carbon atom bound to silicon. [b] D = 3.336×10^{-30} C m.

is clearly polarised $(SiH_3)^-(C_7H_7)^+$, as shown both by the charges, and by the very large dipole moment. In this isomer the occupied π levels of the ring, which would have A_2'' and E_1'' symmetry respectively for a ring in isolation, having binding energies of 13.63 and 11.26 eV respectively: the corresponding values calculated for isolated $C_7H_7^+$ are 18.05 and 15.44 eV. The principal bonding between the pyramidal SiH_3 group and the planar C_7H_7 group in η^7-$SiH_3C_7H_7$ involves interaction of the axial $Si(3p_z)$ orbital with the quasi-A_2'' π orbital of the ring, and the doubly degenerate radial $Si(3p_{x,y})$ orbitals with quasi-E_2'' orbital.

Migration of SiH_3 groups

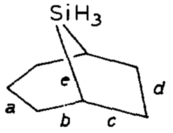
The migration of the SiH_3 group in η^1-$SiH_3C_7H_7$ can, in principle, proceed via three distinct pathways: the [1,2] shift (≡ [1,7]) is the least-motion pathway, and the [1,5] shift (≡ [1,4]) is that predicted on orbital-symmetry grounds. The [1,3] shift (≡ [1,6]) appears to have no factors acting in its favour. Extensive exploration of the potential energy surface in search of transition states for these three re-arrangement pathways revealed only a single saddle-point, corresponding to the [1,5] shift pathway. This is consistent both with the predictions of orbital symmetry, and with the experimental observations on 7-$Ph_3SnC_7H_7$ [12,13]. The structural details for this transition state are given in Table 5; both the bond lengths and the bond orders are indicative of IX as the best single representation. The overall charge carried by the SiH_3 group is only $-0.041e$, and no CH group carries a charge greater in magnitude than $\pm 0.10e$.



(IX)

TABLE 5

STRUCTURE OF THE TRANSITION STATE FOR THE [1,5] MIGRATION OF SiH_3 IN η^1-$SiH_3C_7H_7$



Distances (Å)		*Bond orders*	
a	1.403	*a*	1.423
b	1.431	*b*	1.299
c	1.490	*c*	0.975
d	1.346	*d*	1.899
e	2.131	*e*	0.476
Bond angles (°)		*Dihedral angles (°)*	
aa'	121.8	*aa'/ee'*	112.6
ab	123.9	*aa'/cdc'*	123.5
bc	118.9	*cdc'/ee'*	123.9
cd	117.3		
be	101.6		
ce	95.3		
ee'	79.0		

The calculated $\Delta H_f^{\ominus}$ value this transition state is +294.2 kJ mol^{-1}, some 172 kJ mol^{-1} above the ground state energy for the axial conformer of 7-$SiH_3C_7H_7$: these values refer to isolated gas-phase species in the absence of solvation. Despite the small net charges in the transition state, its dipole moment is very much larger than that of the ground state, 2.87 D as compared with 0.29 D. As we have suggested previously [1] for the analogous cyclopentadiene system, the increased dipole moment of the silylcycloheptatriene transition state, representing increased charge separation, will lead to a substantial increase in solvation in the transition state as compared with the ground state, so reducing the very high isolated-molecule activation energy to a much lower solution activation energy.

Conformational preference in cycloheptatrienes and cyclohexanes

As noted earlier, the more stable conformer of 7-$SiH_3C_7H_7$ is that having the SiH_3 axial: this may be compared with the observed [9] axial conformation of 7-$Ph_3SnC_7H_7$. The same pattern occurs in 7-$CH_3C_7H_7$ with an almost identical energy difference calculated between the axial and equatorial isomers. For comparison we give in Table 6, the calculated $\Delta H_f^{\ominus}$ values not only of the conformers of some 7-substituted cycloheptatrienes but of cyclohexanes also.

As expected in the cyclohexane series, the equatorial conformer is calculated to be the more stable and the energy difference between the conformers increases as the steric demands of the substituent increase. Although the energy difference Δ calculated here for methyl-cyclohexane, 3.5 kJ mol^{-1} is about double the experimental value [22], the qualitative variation of Δ in the cyclohexanes seems plausible.

In contrast to the t-butyl- and trimethylsilyl-cyclohexanes, in the cycloheptatrienes only a single minimum was found, corresponding to the axial conformer. All attempts to find energy minima for the equatorial conformers of 7-$Me_3MC_7H_7$ (M = C, Si) led to the corresponding axial conformers. The dominant conformational influence in 7-substituted cycloheptatrienes appears to be the interaction of the substituent with the hydrogens on carbons 1 and 6, where the distance to an equatorial substituent is much less than that to an axial substituent. This is accentuated by the changes in the ring dihedral angle α (defined in Table 2) with conformer, (Table 7): axial substituents increase α compared with the value in C_7H_8

TABLE 6

ENERGIES OF AXIAL AND EQUATORIAL CONFORMERS IN CYCLOHEPTATRIENES AND CYCLOHEXANES

X	7-C_7H_7X			$C_6H_{11}X$		
	$\Delta H_f^{\ominus}$ (kJ mol^{-1})		Δ^a (kJ mol^{-1})	$\Delta H_f^{\ominus}$ (kJ mol^{-1})		Δ^a (kJ mol^{-1})
	axial	equatorial		axial	equatorial	
CH_3	+134.3	+142.1	−7.8	−146.4	−149.9	+3.5
SiH_3	+121.8	+129.7	−7.9	−150.0	−154.5	+4.5
CMe_3	+148.0	^{b}		−111.6	−127.8	+16.2
$SiMe_3$	−176.3	^{b}		−437.8	−449.6	+11.8

^{a} $\Delta = \Delta H_f^{\ominus}$ (axial) − $\Delta H_f^{\ominus}$ (equatorial). ^{b} No minimum found for equatorial conformer: all optimisations led to axial conformer.

TABLE 7

VARIATION OF CALCULATED RING DIHEDRAL ANGLES IN 7-SUBSTITUTED CYCLOHEPTATRIENES

Substituent	α (°)	β (°)
H	15.2	8.9
CH_3 (axial)	21.8	11.1
CH_3 (equatorial)	7.4	2.7
SiH_3 (axial)	19.7	10.5
SiH_3 (equatorial)	9.9	3.4
CMe_3 (axial)	24.6	11.9
$SiMe_3$ (axial)	21.5	9.6

(cf. the experimental values for C_7H_8 and 7-$Ph_3SnC_7H_7$ in Table 2), whereas equatorial substituents decrease the value of α (similar changes occur also in the value of the dihedral angle β). In 7-$SiH_3C_7H_7$, the distances from the hydrogens at C(1) and C(6) to the 7-Si and 7-H are, in the axial isomer: 3.14 and 2.32 Å, respectively, and in the equatorial isomer: 2.81 and 2.52 Å, respectively. These values are all within the sums of Van der Waals radii [23,24] of (H + Si), 3.55 Å and of (H + H), 2.90 Å: the biggest difference between the calculated distance and the Van der Waals' sum is for the Si ··· H interaction in the equatorial isomer, and this presumably is the dominant factor in establishing the conformational preference.

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