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THE STRUCTURES OF DICYCLOPENTADIENYLSILENES AND RELATED COMPOUNDS

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Summary

The most stable form, according to MNDO calculations, of the silene $(C_5H_5)_2Si$ is the bis-monohapto isomer, in which the angle (CSiC) is 105.4°, and the conformation is such that the dihedral angles δ (HCSiC) are zero. The bis-pentahapto isomer is of comparable energy, and has minimum energy for a structure of D_{5d} symmetry: this isomer does not represent a genuine energy minimum. Entirely similar conclusions result from calculations on the isoelectronic $(C_5H_5)_2P^+$, but for $(C_5H_5)_2Al^-$, although the lowest energy form is again $(\eta^1\text{-}C_5H_5)_2Al^-$, the $(\eta^5\text{-}C_5H_5)_2Al^-$ isomer has only C_{2v} symmetry with angle (XAlX) 151.5°. In the silene derivatives $(\eta^1\text{-}C_5H_5)_2SiCY_2$, the unique SiC interaction is a genuine Si=C double bond and the molecular skeleton C_2SiCY_2 is planar: however in the isomeric species $(\eta^5\text{-}C_5H_5)_2SiCY_2$, which do not represent genuine energy minima, the unique SiC interaction is a long, highly polar bond in a twisted X_2SiCY_2 skeleton in which the X_2SiC and $SiCY_2$ planes are perpendicular.

Introduction

In a recent paper [1] we reported calculations on the energy differences between $(\eta^1\text{-}C_5H_5)SiR_3$ and $(\eta^5\text{-}C_5H_5)SiR_3$: when R = H, the monohapto isomer is the more stable by some 245 kJ mol^{-1}, and when R = Me, the monohapto form is the more stable isomer by some 290 kJ mol^{-1}. In a similar manner $(\eta^1\text{-}C_7H_7)SiH_3$ is more stable [2] than $(\eta^7\text{-}C_7H_7)SiH_3$ by some 325 kJ mol^{-1}. In the present paper we turn to a consideration of the possible structures of dicyclopentadienylsilene $(C_5H_5)_2Si$ and of some related species containing formal silicon–carbon double bonds, of general type $(C_5H_5)_2Si{=}CY_2$. Cowley and co-workers have described [3] briefly some calculations on $(C_5H_5)_2Si$, which were undertaken as a part of a wider study of bent $(C_5H_5)_2M$ systems, from which they have concluded that the global energy minimum for $(C_5H_5)_2Si$ occurs for the bis-pentahapto isomer, and that the various conformations of the bis-monohapto isomer are some 90–110 kJ mol^{-1} higher in

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energy than the bis-pentahapto form. This conclusion is not supported by our own calculations which find $(\eta^1\text{-}C_5H_5)_2Si$ and $(\eta^5\text{-}C_5H_5)_2Si$ to be of essentially the same energy.

Calculations

All calculations were made using the MNDO method, with the published parameterization [4–6]. Molecular energies were calculated for fully optimised geometries, and except as otherwise noted, no geometric assumptions or constraints were made or applied: for the pentahapto systems, local C_{5v} symmetry was applied to $(C_5H_5)Si$ fragments, but no assumptions were made about the geometry at the silicon in these systems. In the determination of the conformation energy map for $(\eta^1\text{-}C_5H_5)_2Si$, the two independent dihedral angles δ(HCSiC) were independently constrained at a series of values at fixed increments between 0 and 360°, while all the remaining geometrical variables were simultaneously optimised: the resulting map had the symmetry of plane group *pmm*. The isoelectronic systems $(C_5H_5)_2Al^-$ and $(C_5H_5)_2P^+$ were treated in an entirely similar way.

Results

The structures of $(C_5H_5)_2Si$ isomers. When local C_{5v} symmetry is imposed upon the individual $(\eta^5\text{-}C_5H_5)Si$ fragments, the resulting optimisation yields a structure of D_{5d} symmetry, in which the C–C and Si–C distances are 1.438 and 2.198 Å respectively, corresponding to bond orders of 1.304 and 0.198: if X represents the centroid of the cyclopentadiene ring, then the Si–X distance is 1.826 Å, and angle (XSiX) is 180°. The D_{5h} conformation is of virtually identical energy (Table 1), indicative of essentially free rotation of the rings, relative to one another. The HOMO, of E_{1g} symmetry in D_{5d} and E_1'' in D_{5h} at -8.55 eV, contains no contribution from silicon, within an (s,p) basis set: the principal ring-silicon bonding involves the silicon p_z orbital, giving an orbital of A_{2u} or A_2'' symmetry at -14.50 eV, and the p_x, p_y orbitals, which give bonding levels of E_{1u} or E_1' symmetry at -10.17 eV. The silicon 3*s* orbital is essentially non-bonding at -16.94 eV.

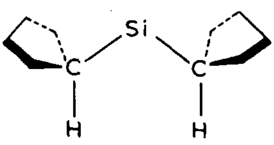
TABLE 1

MOLECULAR ENERGIES FOR ISOELECTRONIC $(C_5H_5)_2M$

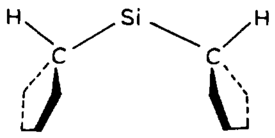
	$\Delta H_f^\ominus$ (kJ mol^{-1})
$(\eta^5\text{-}C_5H_5)_2Si$, D_{5d}	+212.1
$(\eta^5\text{-}C_5H_5)_2Si$, D_{5h}	+212.3
$(\eta^1\text{-}C_5H_5)_2Si$, C_{2v} (I)	+190.3
C_{2v} (II)	+215.7
$(\eta^5\text{-}C_5H_5)_2P^+$, D_{5d}	+1377.0
$(\eta^5\text{-}C_5H_5)_2P^+$ C_{2v} [a]	+1127.9
$(\eta^1\text{-}C_5H_5)_2P^+$ C_{2v} [b]	+1176.8
$(\eta^5\text{-}C_5H_5)_2Al^-$, D_{5d}	+387.9
$(\eta^5\text{-}C_5H_5)_2Al^-$, C_{2v} [c]	+385.0
$(\eta^1\text{-}C_5H_5)_2Al^-$, C_{2v} [a]	+242.6
$(\eta^1\text{-}C_5H_5)_2Al^-$, C_{2v} [b]	+251.8

[a] Conformer like I. [b] Conformer like II. [c] $V = (XAlX) = 151.5°$.

When no geometric constraints are applied to the structure of $(C_5H_5)_2Si$, the optimisation gave a bis-monohapto structure: a large number of possible conformations exist for $(\eta^1\text{-}C_5H_5)_2Si$, and so consequently a conformational energy map was prepared, relating the molecular energy to the two independent rotations about C–Si bonds. This map revealed that the lowest energy conformations was I, and the highest was II.



(I)



(II)

In I the C–Si bond length is 1.832 Å, of bond order 0.764, and the angle (CSiC) is 105.4°: in II, the C–Si bond length is virtually identical at 1.833 Å, but the angle (CSiC) has increased to 114.7°, as the energy has increased by 25.4 kJ mol^{-1}. For comparison, we note that in Me_2Si, the calculated C–Si distance is 1.818 Å (bond order 0.865), and the angle (CSiC) is 103.6°. It seems reasonable to ascribe the energy difference between I and II to the repulsive interaction of the π electrons in the two diene systems of II: the increase in the angle (CSiC) between I and II is consistent with this, as is the overall form of the conformation energy map. Thus conformations intermediate between I and II having overall C_2 symmetry are, for a given magnitude of the dihedral angle δ(HCSiC), of lower energy than those of C_s symmetry; in the C_2 species the diene systems are always further apart than in the corresponding C_s species.

Cowley et al. [3] have reported MNDO calculations on the isomeric forms of $(C_5H_5)_2Si$, from which they conclude that the global energy minimum corresponds to the D_{5d} $(\eta^5\text{-}C_5H_5)_2Si$ structure with the various $(\eta^1\text{-}C_5H_5)_2Si$ some 90–110 kJ mol^{-1} higher. These results are quite at variance with our own findings, based upon the same method. Firstly although Cowley's energy for $(\eta^5\text{-}C_5H_5)_2Si$ ($\Delta H_f^{\ominus}$ +212.4 kJ mol^{-1}) is identical with that given in Table 1, the energies reported [3] for $(\eta^1\text{-}C_5H_5)_2Si$ are far too high ($\Delta H_f^{\ominus}$ values in the range 305.3 to 324.1 kJ mol^{-1}). No conformational energy map appears to have been computed [3] for $(\eta^1\text{-}C_5H_5)_2Si$ and it is not possible to speculate about why the energies of these conformers appear to be so much in error, except to note that some unspecified geometric constraint may have been applied.

Consequently we conclude, contrary to Cowley [3], that in fact the global energy *minimum for* $(C_5H_5)_2Si$ *occurs not for the pentahapto isomer, but for the monohapto isomer in conformation* I. The isomeric $(\eta^5\text{-}C_5H_5)_2Si$, so far from being the global minimum, is not a minimum at all: when the symmetry constraints are released, the calculated geometry undergoes a complex reorganisation to yield $(\eta^1\text{-}C_5H_5)_2Si$, some 22 kJ mol^{-1} below $(\eta^5\text{-}C_5H_5)_2Si$. However, we concur with the conclusion of Cowley et al. [3] that within the constraints of local C_{5v} symmetry applied to each $(C_5H_5)Si$ fragment, the lowest energy occurs at D_{5d} symmetry, but that distortions towards C_{2v} require only a modest energy input: to reduce V = angle (XSiX) from 180 to 150°, for example, requires only 22.6 kJ mol^{-1}.

TABLE 2

OPTIMISED PROPERTIES OF $(C_5H_5)_2Si{=}CY_2$

Y	$(\eta^1\text{-}C_5H_5)_2Si{=}CY_2$					$(\eta^5\text{-}C_5H_5)_2Si{=}CY_2$				
	$\Delta H_f^\ominus$ (kJ mol^{-1})	d(Si=C) (Å)	p(SiC)	q(Si)	q(C)	$\Delta H_f^\ominus$ (kJ mol^{-1})	d(Si=C) (Å)	p(SiC)	q(Si)	q(C)
H	+297.1	1.652	1.825	+0.498	−0.374	+583.6	1.917	0.488	+0.826	+0.073
CH_3	+232.2	1.676	1.735	+0.599	−0.482	+479.0	1.997	0.418	+0.864	−0.031
CN	+497.1	1.684	1.516	+0.790	−0.350	+843.2	1.972	0.410	+0.845	+0.145
$COCH_3$	−47.9	1.679	1.613	+0.738	−0.569	+371.3	1.990	0.431	+0.858	−0.051

Molecules isoelectronic with $(C_5H_5)_2Si$. In view of the above discrepancies for the energies of $(C_5H_5)_2Si$, we have recalculated the structures and energies of the isomers of the isoelectronic $(C_5H_5)_2P^+$, previously studied by Cowley et al. [3,7], and also of the isoelectronic $(C_5H_5)_2Al^-$. Although we agree exactly with the energy calculated by Cowley at al. for the $(\eta^5\text{-}C_5H_5)_2P^+$ having $V = 180°$, their energies for the bis-monohapto conformers are again too high by some 100–150 kJ mol^{-1} (Table 1). The lowest energy for a bis-pentahapto structure occurs when $V = 180°$ (i.e. for D_{5h} or D_{5d}) not when $V < 180°$ (i.e. C_{2v}) as suggested by Cowley [3,7]. All bis-pentahapto forms regardless of the initial magnitude of V, when this constraint is released, relax to one or other of the bis-monohapto conformers, so that the global energy minimum (Table 1) is in fact the bis-monohapto isomer, analogous to I. We note with some interest that Cowley reports as the global minimum a bis-pentahapto isomer, having $V < 180°$, and having an energy identical with that found here for the $(\eta^1\text{-}C_5H_5)_2P^+$ isomer analogous to II, and we suggest, although no structural details were given, that this C_{2v} isomer [3] is in fact a bis-monohapto form rather than a bis-pentahapto isomer. There is no doubt, however, that the most stable form is $(\eta^1\text{-}C_5H_5)_2P^+$ in conformation I, having an angle (CPC) of 111.8°, and d(PC) of 1.719 Å.

Similarly, for $(C_5H_5)_2Al^-$, the lowest energy isomer is the bis-monohapto form with angle (CAlC) of 104.2° and d(AlC) of 1.957 Å, again having the conformation with δ (HCAlC) at zero: the bis-pentahapto form is of higher energy (Table 1), but now the lowest energy form of $(\eta^5\text{-}C_5H_5)_2Al^-$ has V 151.5 rather than 180°, although the skeletal bending potential function is very soft. As before, the bis-pentahapto isomers do not represent genuine minima on the potential energy surface.

Within the constraint of pentahapto bonding for the rings, $(C_5H_5)_2Al^-$, having an angular structure is thus similar to the dicyclopentadienyls of the low electronegativity elements germanium, tin, and lead [8–12], rather than the more electronegative silicon and phosphorus which have linear (V 180°) structures in the bis-pentahapto forms. This structural difference can readily be accounted for by a straightforward extension of an earlier model [13], based upon the second-order Jahn–Teller in which non-bonding electrons on central atoms appear to be stereochemically inactive when the ligands are of relatively low electronegativity, or alternatively, when the central atom is of relatively high electronegativity. In our view, this model [13] provides a reasonably satisfactory interpretation of the structures of main-group $(\eta^5\text{-}C_5H_5)_2M$ species, whereas the so-called "14 Interstitial Electron Rule" [3] appears to us to be based upon conclusions drawn from calculations which are in error; hence its overall validity is questionable.

The structures of $(C_5H_5)_2Si{=}CY_2$. In the lowest energy conformation of $(\eta^1\text{-}C_5H_5)_2Si$ (I) the highest two occupied molecular orbitals at −8.85 eV and −8.96 eV are concentrated in the π(C–C) fragments of the rings, closely followed at −9.41 eV by the silicon lone pair in the CSiC plane: the LUMO is the out of plane Si(3p) orbital. For comparison, in Me_2Si, the silicon lone pair is the HOMO at −9.29 eV, while the LUMO is again the out of plane p orbital. In the pentahapto isomer, the silicon 3s orbital is essentially non-bonding, and the 3p orbitals are all involved in bonding to the rings: consequently, it is to be expected that silaethenes of general type $(C_5H_5)_2Si{=}CY_2$ will be of considerably lower energy when the rings are monohapto than when they are pentahapto.

The optimised values of the salient molecular properties for a range of species

$(C_5H_5)_2Si{=}CY_2$ are given in Table 2. For every example of the group Y studied in this work the $\Delta H_f^\ominus$ value for the bis-monohapto isomer was lower by several hundred kJ mol^{-1} than that of the bis-pentahapto isomer. Furthermore, when the constraint of local C_{5v} symmetry was removed from the $(C_5H_5)Si$ fragments in the $(\eta^5\text{-}C_5H_5)_2Si{=}CY_2$ species, optimisation always led to the corresponding $(\eta^1\text{-}C_5H_5)_2Si{=}CY_2$: the bis-pentahapto isomers do not represent genuine energy minima.

In the $(\eta^1\text{-}C_5H_5)_2Si{=}CY_2$ species, the freely optimised geometry always contained a planar $C_2Si{=}CY_2$ fragment, having a calculated Si=C distance in the range 1.65–1.70 Å with a bond order in the range 1.5–1.8. The $(\eta^5\text{-}C_5H_5)_2Si{=}CY_2$ isomers invariably optimised to structures in which the X_2SiC fragment was exactly perpendicular to the $SiCY_2$ fragment (X represents the centroid of the pentahapto ring): the unique SiC distance, in this series, lies in the range 1.90–2.00Å, with bond orders below 0.5.

When in the bis-monohapto isomers, the double bond was twisted so that the C_2SiC and $SiCY_2$ fragments were exactly perpendicular, the energies rose by 100–200 kJ mol^{-1}: the Si=C bond length typically increased by no more than 0.05 Å, although the SiC bond order fell considerably to 1.195 when $X = H$; 1.060 $(X = CH_3)$; 0.966 $(X = CN)$. In the planar, lowest energy forms of $(\eta^1\text{-}C_5H_5)_2Si{=}CY_2$, the HOMO is a p_π–p_π orbital between silicon and carbon, and these species may be described as genuine silaethenes. There has been considerably controversy [14–19] concerning the value of the Si=C bond length. In an electron diffraction study of $Me_2Si{=}CH_2$, the bond length was reported [15] to be 1.83(4) Å, while in an X-ray study of $(Me_3Si)_2Si{=}C(R)OSiMe_3$ (R = 1-adamantyl) a distance of 1.764(3) Å was found [16]. On the other hand, ab initio calculations at various levels of sophistication [14,17–19], suggest that the value of an unperturbed Si=C distance (as in, for example, $H_2Si{=}CH_2$ or $Me_2Si{=}CMe_2$) is ca. 1.70 Å, with predictable [14] changes occurring with substitution. This conclusion supports the deduction that in $(\eta^1\text{-}C_5H_5)_2Si{=}CY_2$ a normal double bond is present. On twisting the silaethene from the planar to the perpendicular, although the bond distance increases only modestly, the bond order drops to around unity, indicative of complete loss of π character. In the perpendicular forms, the HOMO is an occupied $2p_\pi$ orbital localised on the unique carbon, perpendicular to the $SiCY_2$ plane while the LUMO is a $3p_\pi$ orbital localised on silicon and perpendicular to the plane C_2SiC: accordingly twisting is accompanied by a decrease in the first ionisation energy, as the HOMO is converted from a bonding to a non-bonding orbital, and a marked increase in the polarity of the SiC bond, thus: $(\eta^1\text{-}C_5H_5)_2\overset{+}{Si}\text{–}\overset{-}{C}Y_2$.

In view of the length (ca. 1.70 Å) and bond order (ca. 1.75) of a number Si=C bonds the unique SiC interaction in the bis-pentahapto isomers cannot be described as a double bond: this bond (Table 2) is extremely long and of very low order. When the X_2SiCY_2 fragment is constrained to be planar, the unique SiC distance, rather than decreasing upon π-bond formation, increases by amounts ranging from 0.08 Å when $Y = H$ to 0.25 Å when $Y = CN$. Simultaneously the bond order decreases also.

For each of the optimised (perpendicular) structures of $(\eta^5\text{-}C_5H_5)_2Si{=}CY_2$, the angle $V = (XSiX)$ is in the range 140–150°. When the angle V in isolated $(\eta^5\text{-}C_5H_5)_2Si$ is reduced from 180 to 140°, the highest occupied molecular orbital which involves $Si(3p)$ orbitals, at -10.17 eV, is reduced in symmetry from E_1' in D_{5h} to $A_1 + B_1$ in C_{2v}. Of these orbitals the A_1, at -10.81 eV when V 140°, will point directly along the Si–C direction in $(\eta^5\text{-}C_5H_5)_2SiCY_2$, while the B_1, at -10.06 eV, is perpendicular to the X_2SiC plane: on the other hand the third molecular orbital involving Si($3p$) is altered from A_2'' in D_{5h} to B_2 in C_{2v}, and is essentially non-bonding at -13.40 eV when V 140°. Consequently, in $(\eta^5\text{-}C_5H_5)_2SiCY_2$ the principal π(Si–C) interaction will involve the B_2 orbital of the $(\eta^5\text{-}C_5H_5)_2Si$ fragment and the carbon $2p_\pi$ orbital of the CY_2 fragment, so that the X_2SiC and $SiCY_2$ planes are perpendicular, as calculated above.

As discussed earlier, $(C_5H_5)_2Si$ and all the $(C_5H_5)_2SiCY_2$ species studied here are bis-monohapto isomers: on the other hand, both C_5H_5 and C_5Me_5 form bis-pentahapto compounds with germanium, tin, and lead [8–12], and it is consequently to be expected that for the heavier hetero-ethenes containing $(C_5H_5)_2M$ fragments when M = Ge, Sn or Pb, the structures of $(C_5H_5)_2MCY_2$ will exhibit both pentahapto rings and a perpendicular M–C π-bond. Possible examples of perpendicular π(C–C) bonds have been discussed by Schleyer [20].

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