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JAHN-TELLER EFFECTS IN THE MNDO APPROXIMATION: STRUCTURES OF THE MOLECULAR CATIONS OF SOME SIMPLE ORGANOSILANES

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Summary

The MNDO method gives geometries for the molecular cations of types SiH_3R^+, $SiH_2R_2^+$, $SiHR_3^+$ and SiR_4^+ ($R = CH_3$, $CHCH_2$, CCH, and CN) and for $SiH_3CCSiH_3^+$, $(SiH_3)_2CC(SiH_3)_2^+$, $(SiH_3)_2CCC(SiH_3)_2^+$ and $(SiH_3)_4C^+$ which have symmetries in precise accord with the predictions of the Jahn-Teller effect. The geometries of the neutral parent molecules are reported also.

Introduction

In a previous study [1] of the molecular structures of fluoro- and chlorosilanes Si(H, F, Cl)$_4$ and their molecular cations Si(H, F, Cl)$_4^+$, in the MNDO approximation [2], it was found that the optimised point groups of the neutral molecules conformed precisely to intuitive expectation, and moreover that the optimised point groups of the molecular cations exactly obeyed the predictions of the first-order Jahn-Teller effect. When vertical ionisation of a neutral molecule gave rise to a non-degenerate cation, no change of point-group was found on optimisation of the cation structure: however when such vertical ionisation gave a degenerate cation, optimisation of its structure always caused a change in symmetry, to a sub-group of the neutral molecule point group, by motion along one of the molecular vibrations, always of the appropriate symmetry. If the degeneracy was of symmetry class Γ, the internal motion was along non-totally symmetric vibration contained in $[\Gamma]^2$. In view of this remarkable accord between the predictions, based in group theory, and the results, based in semi-empirical SCF MO theory, we have extended that study to the molecular cations of simple organosilanes, and report the results here.

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Method

All computations were undertaken using MNDO [3] implemented on a VAX 11/780 computer: no assumptions of any kind were made, and energies were minimised with respect to all 3N-6 internal coordinates for each molecule and ion. In Table 1 are recorded molecular energies, optimised point groups and symmetry classes of the HOMO for the neutral molecules, and in Table 2 the energies, symmetries and molecular states of the cations are given. Optimised geometries are listed in Tables 3 and 4. Table 5 contains a comparison of observed [4—10] and calculated SiC distances.

Results and discussion

Point groups

In the series $SiH_n(CH_3)_{4-n}$, when $n = 0, 1, 2$, the conformations of the methyl groups are such as to maximise the overall molecular symmetry: in $SiH_2(CH_3)_2$ the methyl groups have four close and two distant hydrogens, and they are very slightly tilted away from one another; in $SiH(CH_3)_3$ each methyl group has one C—H bond parallel to the molecular C_3 axis and to each other with three other pairs of C—H bonds in different methyl groups also parallel. In $Si(CH_3)_4$ the methyl groups describe exact T_d symmetry, and the conformation in $SiH(CH_3)_3$ is precisely derived from T_d $Si(CH_3)_4$ by removal of any one methyl group and its substitution by hydrogen.

SiH_3CHCH_2 has C_s symmetry as expected, but $SiH_2(CHCH_2)_2$ has C_2 rather than the C_{2v} which might have been expected: the effect of the concerted rotation of the vinyl groups both in this molecule, and in $SiH(CHCH_2)_3$ which

(continued on p. 15)

TABLE 1

ENERGIES AND OPTIMISED POINT GROUPS OF NEUTRAL MOLECULES

Molecule	ΔH_f^0 (kJ mol^{-1})	Point group	HOMO
SiH_3CH_3	—64.5	C_{3v}	A_1
$SiH_2(CH_3)_2$	—173.2	C_{2v}	B_2
$SiH(CH_3)_3$	—277.3	C_{3v}	E
$Si(CH_3)_4$	—375.9	T_d	T_2
SiH_3CHCH_2	+26.8	C_s	A''
$SiH_2(CHCH_2)_2$	+9.2	C_2	B
$SiH(CHCH_2)_3$	—0.2	C_3	A
$Si(CHCH_2)_4$	—5.5	D_{2d}	E
SiH_3CCH	+153.4	C_{3v}	E
$SiH_2(CCH)_2$	+265.0	C_{2v}	B_2
$SiH(CCH)_3$	+381.4	C_{3v}	A_1
$Si(CCH)_4$	+501.9	T_d	T_1
SiH_3CN	+50.3	C_{3v}	E
$SiH_2(CN)_2$	+64.0	C_{2v}	B_2
$SiH(CN)_3$	+87.8	C_{3v}	A_1
$Si(CN)_4$	+120.2	T_d	T_2
SiH_3CCSiH_3	+70.9	D_{3d}	E_u
$(SiH_3)_2CC(SiH_3)_2$	—84.9	D_2	B_3
$(SiH_3)_2CCC(SiH_3)_2$	—15.2	D_{2d}	E
$(SiH_3)_4C$	—161.6	T_d	T_2

TABLE 2

ENERGIES AND OPTIMISED POINT GROUPS OF MOLECULAR CATIONS

Ion	ΔH_f^0 (kJ mol^{-1})	Point group	Molecular state
$SiH_3CH_3^+$	+967.1	C_{3v}	$^2A_1$
$SiH_2(CH_3)_2^+$	+845.2	C_{2v}	$^2B_2$
$SiH(CH_3)_3^+$	+721.8	C_s	$^2A'$
$Si(CH_3)_4^+$	+637.6	D_2	$^2B_1$
$SiH_3CHCH_2^+$	+940.8	C_s	$^2A''$
$SiH_2(CHCH_2)_2^+$	+924.6	C_2	^2B
$SiH(CHCH_2)_3^+$	+923.0	C_3	^2A
$Si(CHCH_2)_4^+$	+892.1	D_2	$^2B_1$
SiH_3CCH^+	+1159.4	C_s	$^2A''$
$SiH_2(CCH)_2^+$	+1265.0	C_{2v}	$^2B_2$
$SiH(CCH)_3^+$	+1375.9	C_{3v}	$^2A_1$
$Si(CCH)_4^+$	+1526.0	D_{2d}	$^2B_2$
SiH_3CN^+	+1175.1	C_s	$^2A''$
$SiH_2(CN)_2^+$	+1242.5	C_{2v}	$^2B_2$
$SiH(CN)_3^+$	+1320.6	C_{3v}	$^2A_1$
$Si(CN)_4^+$	+1447.1	D_{2d}	$^2B_2$
$SiH_3CCSiH_3^+$	+1048.6	C_{2h}	^2B_u
$(SiH_3)_2CC(SiH_3)_2^+$	+758.7	D_2	$^2B_3$
$(SiH_3)_2CCC(SiH_3)_2^+$	+798.2	D_2	$^2B_1$
$(SiH_3)_4C^+$	+813.7	D_{2d}	$^2B_2$

TABLE 3

OPTIMISED GEOMETRIES FOR NEUTRAL MOLECULES [a]

SiH_3CH_3	HSi, 1.438; SiC, 1.838; CH, 1.106; HSiC, 110.7; SiCH, 110.9
$SiH_2(CH_3)_2$	HSi, 1.441; SiC, 1.843; CH, 1.106; CSiC, 113.4; HSiC, 109.1; SiCH, 110.3 (X2), 111.4 (X4)
$SiH(CH_3)_3$	HSi, 1.445; SiC, 1.849; CH, 1.106; HSiC, 107.4; SiCH, 111.1
$Si(CH_3)_4$	SiC, 1.857; CH, 1.105; SiCH, 111.2
SiH_3CHCH_2	HSi, 1.438 (X1), 1.439 (X2); SiC(1), 1.801; C(1)C(2), 1.336; C(1)H, 1.095; C(2)H (*trans*), 1.091; C(2)H(*cis*), 1.090; HSiC, 109.7 (X 1), 110.4 (X2); SiC(1)C(2), 127.0; SiC(1)H, 114.3; C(1)C(2)H(*trans*), 123.2; C(1)C(2)H(*cis*), 123.7; HSiC(1)C(2), 180.0 (X1), ±60.1
$SiH_2(CHCH_2)_2$	HSi, 1.442; SiC(1), 1.807; C(1)C(2), 1.336; C(1)H, 1.094; C(2)H(*trans*), 1.091; C(2)H(*cis*), 1.090; HSiH, 107.7; CSiC, 112.7; SiC(1)C(2), 127.3; SiC(1)H, 118.7; C(1)C(1)H(*trans*), 123.2; C(1)C(2)H(*cis*), 123.8; C(2)C(1)SiX, 114.4 (X = point on C_2 axis)
$SiH(CHCH_2)_3$	HSi, 1.447; SiC(1), 1.814; C(1)C(2), 1.335; C(1)H, 1.096; C(2)H(*trans*), 1.091; C(2)H(*cis*), 1.090; HSiC, 106.6; SiC(1)C(2), 129.4; SiC(1)H, 118.4; C(1)C(2)H(*trans*), 123.1; C(1)C(2)H(*cis*), 124.1; C(2)C(1)SiH, 142.5
$Si(CHCH_2)_4$	SiC(1), 1.823; C(1)C(2), 1.336; C(1)H, 1.094; C(2)H(*trans*), 1.091; C(2)H(*cis*), 1.090; CSiC, 109.5; SiC(1)C(2), 126.9; SiC(1)H, 114.9; C(1)C(2)H(*trans*), 123.1; C(1)C(2)H(*cis*), 124.0
SiH_3CCH	HSi, 1.439; SiC, 1.743; CC, 1.202; CH, 1.052; HSiC, 109.0
$SiH_2(CCH)_2$	HSi, 1.443; SiC, 1.747; CC, 1.201; CH, 1.052; HSiH, 110.2; CSiC, 109.9
$SiH(CCH)_3$	HSi, 1.447; SiC, 1.751; CC, 1.201; CH, 1.052; HSiC, 109.2
$Si(CCH)_4$	SiC, 1.756; CC, 1.200; CH, 1.052
SiH_3CN	HSi, 1.438; SiC, 1.755; CN, 1.165; HSiC, 107.8
$SiH_2(CN)_2$	HSi, 1.442; SiC, 1.755; CN, 1.164; HSiH, 113.0; CSiC, 107.8
$SiH(CN)_3$	HSi, 1.446; SiC, 1.756; CN, 1.164; HSiC, 110.4
$Si(CN)_4$	SiC, 1.756; CN, 1.163
SiH_3CCSiH_3	HSi, 1.439; SiC, 1.745; CC, 1.209; HSiC, 109.0
$(SiH_3)_2CC(SiH_3)_2$	HSi, 1.439; SiC, 1.817; CC, 1.332; HSiC 109.9 (X4), 110.2 (X4), 111.5 (X4); SiCC, 124.0; Si(4)C(2) planar; twist of SiH_3, 34.7
$(SiH_3)_2CCC(SiH_3)_2$	HSi, 1.439 (X8), 1.438 (X4); SiC, 1.805; CC, 1.304; HSiC, 109.5 (X8), 111.1 (X4); SiCC, 121.7
$(SiH_3)_4C$	CSi, 1.836; SiH, 1.439; CSiH, 110.6

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[a] Distances XY in Å; bond angles XYZ and torsional angles WXYZ in degrees.

TABLE 4

OPTIMISED GEOMETRIES FOR MOLECULAR CATIONS [a]

$SiH_3CH_3^+$	HSi, 1.443; SiC, 2.080; CH, 1.099; HSiC, 99.4; SiCH, 99.7
$SiH_2(CH_3)_2^+$	HSi, 1.438; SiC, 1.923; CH, 1.121 (X2), 1.099 (X4); CSiC, 99.1; HSiC, 111.2; SiCH, 89.9 (X2), 112.8 (X4)
$SiH(CH_3)_3^+$	HSi, 1.440; SiC(1), 2.048(X1); SiC(2), 1.845 (X2); C(1) H_a, 1.096 (X1); C(1) H_b, 1.102 (X2); C(2) H_c, 1.103 (X2); C(2) H_d, 1.103 (X2); C(2) H_e, 1.118 (X2); HSiC(1), 104.9 (X1); HSiC(2), 112.3 (X2); C(1)SiC(2), 103.9 (X2); C(2)SiC(2'), 117.9 (X1); SiC(1) H_a, 107.6 (X1); SiC(1) H_b, 98.7 (X2); SiC(2) H_c, 113.7 (X2); SiC(2) H_d, 114.6 (X2); SiC(2) H_e, 101.4 (X2): C(1)H_a, C(2)H_c approximately parallel to HSi; $H_d \cdots H_d$, 4.968; $H_e \cdots H_e$, 3.192)
$Si(CH_3)_4^+$	SiC, 1.890; CH, 1.101 (X4), 1.107 (X8); CSiC, 118.7 (X2), 105.2 (X4); SiCH, 115.2 (X4); 105.2 (X8): CH_3 groups twisted by 2.5° from D_{2d} to D_2.
$SiH_3CHCH_2^+$	HSi, 1.438 (X1), 1.445 (X2); SiC(1), 1.827; C(1)C(2), 1.395; C(1)H, 1.102; C(2)H(*trans*), 1.096; C(2)H(*cis*), 1.094; HSiC, 106.9 (X1); 106.3 (X1); 102.9 (X1); SiC(1)C(2), 127.4; SiC(1)H, 114.5; C(1)C(2)H(*trans*), 121.2; C(1)C(2)H(*cis*), 122.9; HSiC(1)C(2), 180.0, ±58.8
$SiH_2(CHCH_2)_2^+$	HSi, 1.440; SiC(1), 1.819; C(1)C(2), 1.362; C(1)H, 1.096; C(2)H(*trans*), 1.095; C(2)H(*cis*), 1.092; HSiH, 113.8; CSiC, 99.8; SiC(1)C(2), 127.0; SiC(1)H, 120.2; C(1)C(2)H(*trans*), 121.9; C(1)C(2)H(*cis*), 124.1; C(2)C(1)SiX, 89.9 (X = point on C_2 axis).
$SiH(CHCH_2)_3^+$	HSi, 1.482; SiC(1), 1.802; C(1)C(2), 1.359; C(1)H, 1.096; C(2)H(*trans*), 1.092; C(2)H(*cis*), 1.090; HSiC, 103.9: SiC(1)C(2), 129.8; SiC(1)H, 117.2; C(1)C(2)-(*trans*), 122.1; C(1)C(2)H(*cis*), 124.1; C(2)C(1)SiH, 102.1
$Si(CHCH_2)_4^+$	SiC(1), 1.822; C(1)C(2), 1.352; C(1)H, 1.093; C(2)H(*trans*), 1.092; C(2)H(*cis*), 1.089; CSiC, 112.2 (X2), 109.4 (X2), 106.8 (X2); SiC(1)C(2), 126.7; SiC(1)H, 114.3; C(1)C(2)H(*trans*), 121.6; C(1)C(2)H(*cis*), 123.9
SiH_3CCH^+	HSi, 1.443 (X1), 1.471 (X2); SiC, 1.735; CC, 1.258; CH, 1.064; HSiC, 109.1 (X1), 105.5 (X2); HSiH, 104.1 (X1), 115.7 (X2)
$SiH_2(CCH)_2^+$	HSi, 1.475; SiC, 1.726; CC, 1.228; CH, 1.059; HSiH, 105.3; CSiC, 111.3; SiCC, 178.5
$SiH(CCH)_3^+$	HSi, 1.499; SiC, 1.732; CC, 1.218; CH, 1.058; HSiC, 104.9; SiCC, 179.5
$Si(CCH)_4^+$	SiC, 1.750; CC, 1.219; CH, 1.057; CSiC, 110.5 (X2), 109.0 (X4)
SiH_3CN^+	HSi, 1.455 (X1), 1.540 (X2); SiC, 1.708; CN, 1.171; HSiC, 119.2 (X1), 112.4 (X2): HSiH, 56.9 (X1), 119.5 (X2)
$SiH_2(CN)_2^+$	HSi, 1.538; SiC, 1.716; CN, 1.178; HSiH, 82.0; CSiC, 113.4
$SiH(CN)_3^+$	HSi, 1.577; SiC, 1.733; CN, 1.174; HSiC, 103.2
$Si(CN)_4^+$	SiC, 1.758; CN, 1.174; CSiC, 112.6 (X2), 107.9 (X4)
$SiH_3CCSiH_3^+$	HSi, 1.444 (X2), 1.452 (X4); SiC, 1.751; CC, 1.266; HSiC, 107.3 (X2), 105.2 (X4)
$(SiH_3)_2CC(SiH_3)_2^+$	HSi, 1.438 (X8), 1.441 (X4); SiC, 1.855; CC, 1.320; HSiC, 106.1; SiCC, 125.1; SiCCSi, 51.2; twist of SiH_3, 2.8°
$(SiH_3)_2CCC(SiH_3)_2^+$	HSi, 1.436 (X4), 1.438 (X4), 1.440 (X4); SiC, 1.836; CC, 1.309; HSiC, 107.2 (X4), 106.3 (X4), 105.8 (X4); SiCC, 123.1; HSiCSi, 179.7 (X4), 59.8 (X4), 299.5 (X4)
$(SiH_3)_4C^+$	CSi, 1.871; SiH, 1.441; CSiC, 124.0 (X2), 103.4 (X4); CSiH, 104.4 (X8), 111.4 (X4)

TABLE 5

OBSERVED AND CALCULATED Si—C DISTANCES

Molecule	d(SiC) (Å)		Ref.
	Observed	Calculated	
SiH_3CH_3	1.867	1.838	4
$SiH_2(CH_3)_2$	1.867	1.843	5
$SiH(CH_3)_3$	1.868	1.849	6
$Si(CH_3)_4$	1.879	1.857	7
SiH_3CHCH_2	1.853	1.801	8
SiH_3CCH	1.826	1.743	9
SiH_3CN	1.858	1.755	10

has exact C_3 symmetry, is to reduce the H···H repulsions between the vinyl groups. For C_{2v} or C_{3v} respectively there are a number of close H···H contacts between substituents. $Si(CHCH_2)_2$ has D_{2d} symmetry.

The molecules $SiH_n(CX)_{4-n}$ (X = N, CH throughout this paper); have symmetry C_{3v}, C_{2v}, C_{3v} or T_d, according as $n = 3, 2, 1, 0$.

Of the polysilyl species, SiH_3CCSiH_3 has the expected D_{3d} symmetry and in $C(SiH_3)_4$ the conformation defines exact T_d symmetry. In the alkene $(SiH_3)_2CC(SiH_3)_2$ the symmetry is D_2: the Si_4C_2 skeleton is planar and the conformation of silyl groups is such that one Si—H bond in each group is approximately normal to the Si_4C_2 plane. In contrast the allene $(SiH_3)_2CCC(SiH_3)_2$ has full D_{2d} symmetry with four close and two distant hydrogens between the silyl groups on a common carbon atom.

Upon ionisation, all species in which the HOMO for the neutral molecule is degenerate, are found to undergo a change in point group, while those in which the neutral molecule HOMO is non-degenerate all retain the same point group, although of course with changed molecular dimensions. Thus in $HSi(CH_3)_3^+$, only one mirror plane of the C_{3v} operators is retained, so that the ion contains two distinct SiC distances and two distinct HSiC angles (see Table 4). In $Si(CH_3)_4^+$ the tetrahedron SiC_4 is flattened somewhat to D_{2d}, and the CH_3 groups are rotated, so lowering the overall symmetry to D_2.

In $Si(CHCH_2)_4^+$, the symmetry is lowered from the D_{2d} of the neutral parent to D_2. The four SiC bonds are still of the same length, but the two CSiC planes are no longer perpendicular. In both SiH_3CCH^+ and SiH_3CN^+ the symmetry is lowered from C_{3v} to C_s by virtue of a tilt of the SiH_3 group such that its axis is no longer coincident with the SiCX direction. In both $Si(CX)_4^+$ ions, the tretrahedral SiC_4 group found in the neutral parents is flattened, lowering the symmetry to D_{2d}.

In $SiH_3CCSiH_3^+$, a concerted tilt of the SiH_3 groups retains the centre of inversion but lowers the symmetry to C_{2h}, while a concerted tilt of the silyl groups in $(SiH_3)_2CCC(SiH_3)_2^+$ reduces the symmetry from D_{2d} to D_2. $C(SiH_3)_4$ retains D_{2d} symmetry, unlike $Si(CH_3)_4^+$: the CSi_4 skeleton is flattened, on ionisation, from tetrahedral to D_{2d}, but no rotation of the SiH_3 groups occurs.

Molecular dimensions

Previous studies of silicon compounds by the MNDO method [1,11] have shown that, by comparison with experimental molecular dimensions, the calculated values of Si—H distances are systematically ca. 3% too small, while those for Si—F and Si—Cl are too large, by about the same percentage. However the variations of bond distances within series of molecules are well reproduced. It is interesting therefore to extend this comparison of observed and calculated values to the simple organosilanes, (Tables 3 and 5): as usual, Si—H distances have calculated values systematically too short. A comparison of values for Si—C distances is made in Table 5, from which several points emerge. As with Si—H bonds, Si—C bonds are uniformly calculated to be too short, again by some 2—4%: calculated distances to four-coordinate carbon exceed those to three-coordinate carbon which in turn exceed those to two-coordinate carbon, as expected. In the pair SiH_3CN and SiH_3CCH, the Si—C distance in the nitrile is both calculated, and observed, to exceed that in the alkyne: similar values are found also in Me_3SiCN, 1.844 Å [12] and Me_3SiCCH, 1.827 [13]. Although there is a systematic underestimate by MNDO of Si—C distances the ordering of molecules in terms of Si—C distance is correct.

Consequently, although both Si—H and Si—C distances calculated in the molecular cations are probably low by some 3% on average, the changes in the distances which are calculated to occur as a result of ionisation are reliable. In the series $SiH_n(CH_3)_{4-n}$, ionisation causes only modest changes to Si—H and C—H distances, but substantial increases in Si—C: 0.242 Å in SiH_3CH_3, 0.080 Å in $SiH_2(CH_3)_2$, a mean increase of 0.064 Å in $SiH(CH_3)_3$, and 0.033 Å in $Si(CH_3)_4$. In the series $SiH_n(CHCH_2)_{4-n}$, ionisation effects only slight changes, less than 0.02 Å, in Si—C, but causes a uniform increase in C—C: similarly in $SiH_n(CCH)_{4-n}$, the major change upon ionisation is an increase in the C—C distance. On the other hand in the isoelectronic series $SiH_n(CN)_{4-n}$, ionisation causes no significant change in the C—N distance, but causes an increase, typically around 0.1 Å, in Si—H, and a decrease in Si—C varying from 0.047 Å in SiH_3CN via 0.039 and 0.023 Å in $SiH_2(CN)_2$ and $SiH(CN)_3$, respectively, to no change in $Si(CN)_4$. In both $(SiH_3)_2CC(SiH_3)_2$ and $(SiH_3)_2CCC(SiH_3)_2$, the principal dimensional change on ionisation is an increase in the Si—C distance, 0.038 and 0.031 Å, respectively.

Electronic structures

The changes both in molecular dimensions, and in point groups, consequent upon ionisation can be understood to some extent in terms of electronic structure, in particular in terms of the identity of the HOMO. In $SiH_n(CH_3)_{4-n}$, the HOMO is concentrated in the Si—C bonds, so that they become longer and weaker on ionisation: the SiC_{4-n} skeleton is also expected to be strongly Jahn-Teller distorted in those cases where the HOMO is degenerate. In both SiH_n-$(CHCH_2)_{4-n}$ and $SiH_n(CCH)_{4-n}$ the HOMO is concentrated in the C—C bonds, e.g. in $Si(CCH)_4$ the HOMO is of T_1 symmetry, whereas in all other T_d species it is T_2: hence the major geometric changes, consequent upon ionisation, are to be expected in the C—C fragments rather than in the SiC_n fragments: only rather weak Jahn-Teller distortions of the SiC_n skeletons are to be expected. Of the series $SiH_n(CH)_{4-n}$, only in $Si(CN)_4$ does the HOMO contain a significant contribution from the nitrogen lone pairs: in the remainder the HOMO is concentrated in the HSiC fragments, leading an ionisation to dimensional change in Si—H and Si—C and a strong Jahn-Teller distortion in SiH_3CN^+.

Jahn-Teller effect

The data of Tables 1 and 2 indicate that for molecules in which the HOMO is non-degenerate, the corresponding molecular cation has the same point group as its neutral parent, without exception. A reduction in symmetry always occurs, however, when the neutral parent has degenerate HOMO. In Table 6 are given the possible modes of distortion for the appropriate symmetries of HOMO found in this study (Table 1). The direct products $[\Gamma]^2$ generally span more than one non-totally symmetric class, and with one exception, molecular vibrations occur in these molecules in all classes spanned by $[\Gamma]^2$: the sole exception is SiH_3CCSiH_3 which has no A_{2g} vibration. There is thus (Table 6) a choice of distortion modes corresponding to motion along

TABLE 6

JAHN-TELLER EFFECT

Point group	HOMO	Possible distortions	Observed distortions	Examples
T_d	T_1	$E \rightarrow D_{2d}$ or D_2 $T_1 \rightarrow C_3$ $T_2 \rightarrow C_{3v}$ or C_{2v}	D_{2d}	$Si(CCH)_4^+$
T_d	T_2	$E \rightarrow D_{2d}$ or D_2 $T_1 \rightarrow V_3$ $T_2 \rightarrow C_{3v}$ or C_{2v}	D_2 D_{2d}	$Si(CH_3)_4^+$ $\{C(SiH_3)_4^+$ $Si(CN)_4^+$
D_{3d}	E_u	$[A_{2g} \rightarrow S_6$ or $C_3]$ [a] $E_g \rightarrow C_{2h}$, C_2 or C_3	C_{2h}	$SiH_3CCSiH_3^+$
D_{2d}	E	$A_2 \rightarrow S_4$ $B_1 \rightarrow D_2$ $B_2 \rightarrow C_{2v}$	D_2	$\{Si(CHCH_2)_4^+$ $(SiH_3)_2CCC(SiH_3)_2^+$
C_{3v}	E	$A_2 \rightarrow C_3$ [b, c] $E \rightarrow C_s$	C_s	SiH_3CCH^+ SiH_3CN^+ $SiH(CH_3)_3^+$

[a] No A_{2g} vibration occurs in SiH_3CCSiH_3. [b] No A_2 vibration occurs in SiH_3CCH or SiH_3CN. [c] See text.

one of several vibrations. Without exception the optimised geometry of the molecular cations carresponds to one of the geometries predicted by the Jahn-Teller effect, usually to that which retains the highest symmetry. In C_{3v} two possible distortions may occur in $SiH(CH_3)_3$: motion along an E vibration of the SiC_3 skeleton reduces the symmetry to C_s and this is in fact the motion observed; there are also two vibrations of A_2 symmetry involving concerted rocking and twisting of the methyl groups. These vibrations only lower the overall symmetry from C_{2v} to C_3 and it is probable that the HOMO would remain degenerate after such a motion, and a further distortion would then occur lowering the overall molecular symmetry to C_1.

Conclusion

In the present application, MNDO has calculated neutral molecule geometries for a range of organosilanes with rigorously exact symmetry and excellent metrical agreement with experiment, and has found rigorously exact Jahn-Teller distortions in electronically degenerate molecular cations. These results have been achieved in an (s, p) basis of valence electrons only: all the characteristic geometrical properties of simple silanes can be achieved [1,11] within this basis without recourse to Si(3d) orbitals.

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