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AM1 and PM3 semiempirical molecular orbital study of silatranes

III. 1-chlorosilatrane

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Abstract

The AM1 and PM3 semiempirical models have been employed to study the bonding and structure of 1-chlorosilatrane using full geometry optimization. The heats of formation were calculated at different Si–N distances between 200 and 360 pm. Two minima have been found on the energy profile when C_3 symmetry was retained. A third local energy minimum has been found, in an asymmetrical conformation. The energy cost of shortening the Si–N distance has been found to be small; the energy hypersurface is rather flat, with the silatrane skeleton being flexible. The calculations show that the crystal forces could easily distort the gas-phase structure. The comparison of the published X-ray diffraction structure with the calculated geometry and with the experimental geometries of other silatranes leads to the conclusion that the ethoxy links should be disordered.

1. Introduction

The previous papers have reported the MNDO, AM1 and PM3 equilibrium conformations of 1-fluorosilatrane and 1-methylsilatrane [1,2]. Silatranes ($RSi(OCH_2CH_2)_3N$, 1-organyl-2,8,9-trioxa-5-aza-1-silatricyclo [$3.3.3.0^{1.5}$] undecanes) are biologically active silicon-containing organic molecules (Fig. 1) [3–5]. The most interesting structural feature of these molecules is the transannular Si–N donor–acceptor bond. Two basic forms of the structure are possible: the *endo* form in which the lone pair of the nitrogen is turning towards the silicon and the Si–N distance is relatively short (Fig. 1) and the *exo* form in which the nitrogen lone pair is outside and the Si–N distance is much longer (Fig. 2).

In crystalline samples of many substituted silatranes, short Si–N distances were observed. Gas-phase electron diffraction (ED) measurements predict longer Si–N distances for example in 1-fluorosilatrane (204.2 pm (X-ray diffraction (XD)) [6], compared with 232.4 pm (ED) [7]) and in 1-methylsilatrane (217.5 pm (XD) [8], compared with 245 pm (ED) [9]). In 1-chlorosilatrane the Si–N distance is 202.3 pm (XD) [10]; this is the shortest Si–N distance to have been measured, and no ED data are available. The measured Si–N distances are longer than the sum of the covalent radii (187 or 189.5 pm) [11,12] but shorter than the sum of the appropriate non-bonded radii (269 pm) [12] and much shorter than the sum of the Van der Waals radii (350 pm) [11]. The Si–N distance is also variable in solution, shortening in polar solvents and lengthening in non-polar solvents [9]. The Si–N distance has been found to be dependent on the nature of substituent R. An electron-withdrawing substituent (R ≡ fluorine or chlorine) shortens the Si–N distance by decreasing the electron density on silicon and in this way increasing its electron acceptor potential and leading to a stronger Si–N dative bond. This is in agreement with the experimental results. The methyl substitution has an opposite effect, resulting in a longer Si–N bond. This bond lengthening is about 13 pm in both types of measurement.

The silatrane skeleton has been found to have an approximate C_3 symmetry in the solid state. This symmetry is only approximate because of the high flexibility of the ethoxy links [6,8,10]. A partially disordered structure has been found in 1-fluorosilatrane [6]. Nuclear magnetic resonance (NMR) data also show very

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fast ring inversions in solution [13] for other substituted silatranes. The existence of different polymorphic modifications has been explained by the freezing of intramolecular movements.

The high dipole moments of silatranes may play a role in their biological activity by facilitating penetration of membranes [3]. The experimental dipole moment of 1-methylsilatrane is 5.3 D [14].

The early theoretical investigations of silatranes were limited by the size of the molecule, the lack of experimental geometries, its conformational flexibility, the limited methods then available for geometry optimization and the lack of computing power. The nature of the Si–N bond was frequently discussed on the basis of sp^3d hybridization. However, based on the existence of the corresponding boron compound, the boratrane [3], the importance of d orbitals was questioned and another so-called hypervalent model was also proposed [15].

Simple model compounds of neutral pentacoordinated adducts were calculated with full geometry optimization at the *ab-initio* level. The predicted stabilization energies of the NH_3–SiF_4 adduct was calculated to be 10.0 kcal mol^{-1} and 8.6 kcal mol^{-1}, respectively with the minimal and the double-zeta basis set [16,17].

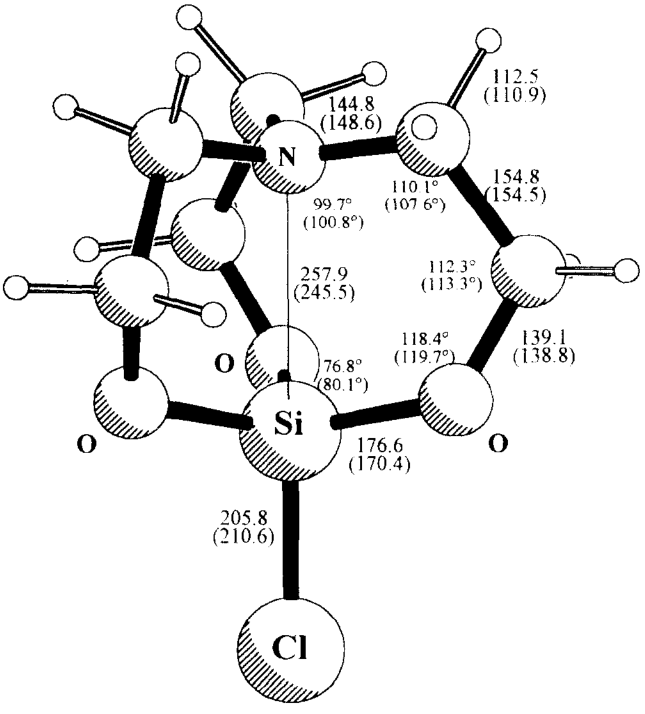

Fig. 1. The molecular diagram of AM1 (PM3) C_3 *endo* equilibrium geometry of 1-chlorosilatrane. The heteroatoms are labelled. The bond distances are in pm and bond angles are in degrees.

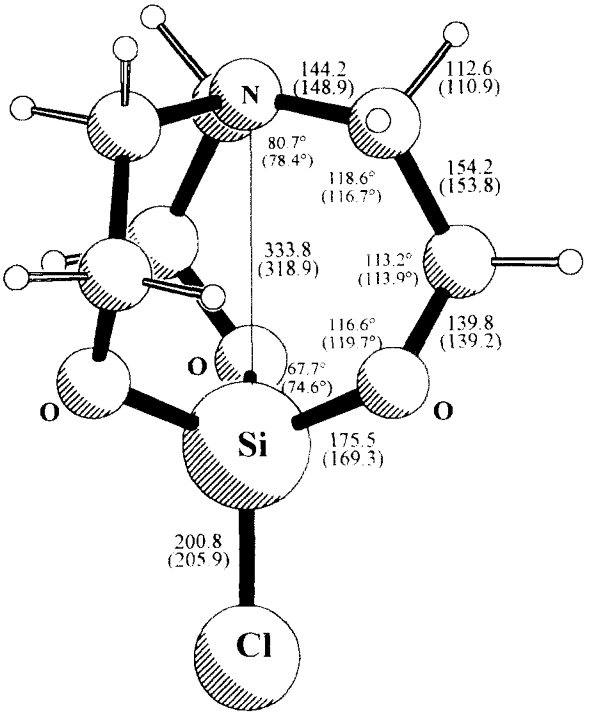

Fig. 2. The molecular diagram of AM1 (PM3) C_3 *exo* equilibrium geometry of 1-chlorosilatrane. The heteroatoms are labelled. The bond distances are in pm and the bond angles are in degrees.

The existence of the NH_3–SiF_4 adduct was proved by experience [18]. A number of *ab initio* calculations show the existence and stability of neutral pentacoordinated compounds containing a silicon–nitrogen bond [19–21]. The axial bond was found to be a three-centre four-electron bond; consequently the strength of the axial Si–N bond is influenced by the ligand in the opposite axial position [21].

Gordon *et al.* [22] used the AM1 semiempirical method to optimize fully the geometry of 1-hydroxysilatrane (R=OH) and related compounds and they performed single-point HF/6-31G(d) *ab initio* calculations in the AM1 equilibrium geometries. The geometries of some simpler model compounds were optimized at the 6-31G(d) *ab initio* level. This permitted direct comparison of *ab initio* and AM1 geometries, and AM1 was found to be satisfactory. The predicted Si–N distances are 15–20 pm longer and the Si–O distances are 6–9 pm longer than the *ab initio* results, but the general trends are well reproduced. On utilization of the Bader [23] electron density analysis, it was found that the Si–N bond critical point still exists at larger Si–N distances; only a small amount of energy is required to decrease the Si–N distance in 1-hydroxysilatrane to reach a typical crystal geometry and, as the number of ethoxy bridges increases, the Si–N bond weakens and the Si–O_{ax} bond strengthens.

Greenberg *et al.* [24] studied the 1-methylsilatrane and model compounds by the HF/3-21G(d) *ab initio* theory. Single-point calculations were performed without any geometry optimization; a solid-state (XD) geometry and an approximate gas-phase geometry were applied. It was found that the Mulliken charges do not change much as the Si–N distance is varied; the silicon is strongly positive and the nitrogen is strongly negative.

In the present paper the results for 1-chlorosilatrane are summarized. Two recent semiempirical model Hamiltonians were used in order to study the effects of parametrization, their utility and limitations.

2. Computational methods

All geometries were fully optimized with the semiempirical AM1 [25] and PM3 [26] methods using adapted versions of the MOPAC [27] program. The latest AM1 parameters for silicon were used [28] in the calculations. The calculations were carried out on an i486/33 MHz workstation and on an IBM RS/6000 model 320H. The PLUTON program was used to plot geometries.

No symmetry constraints were imposed during the geometry optimizations and the precise keyword of MOPAC has always been used. A C_3-like geometry and a completely asymmetric geometry were optimized separately. The Si–N distance was varied between 220 and 360 pm in steps of 20 pm, and other geometrical parameters were fully optimized in each step. Geometry optimizations were then performed, starting from the minimal energy points. The fully optimized geometries were always verified as minima by establishing that their Hessian matrices are positive definite. Frequency analysis was performed, and zero-point energy was calculated in the minimum.

The O–Si–N–C dihedral angle was varied between −20° and 20° in steps of 10°. In this case the Si–N distance was relaxed together with the other geometrical parameters. The energy barrier of the ethoxy flip-flop was also calculated in the minimum, to study the flexibility of the three bridges. Mulliken charges, dipole moments, bond orders and energy partitioning were also calculated.

3. Results and discussion

The Si–N distance 1-chlorosilatrane is expected to be longer than the corresponding distance in 1-fluorosilatrane. This supposition is based on chlorine's smaller electronegativity. The XD results [10] show the opposite behaviour and the Si–N distance is slightly (2 pm) shorter in 1-chlorosilatrane than in 1-fluorosilatrane. Unfortunately no ED measurements are available to show whether this effect is present in the gas phase. The quantum-chemical calculations may help us to understand this behaviour, as it was found that they reproduce the main effects correctly, they give a detailed insight into the molecular structure and they model the effects not easily amenable to experiment. The basic model may be an intramolecular S_N2 reaction in which the N is approaching the Si and the group on the opposite side is leaving. The chlorine is better leaving the group than the fluorine and this may explain the shorter Si–N distance in the case of 1-chlorosilatrane. Table 1 lists the AM1 heats of formation, dipoles and other important calculated values for 1-chlorosilatrane. The geometry has an approximate C_3 symmetry (Figs. 1 and 2). The heat of formation shows two minima as a function of Si–N distance. The *endo* structure is the more stable by 1.4 kcal mol^{-1}. The equilibrium Si–N distances (*endo* and *exo*) are 3–4 pm longer than the corresponding distances calculated in

TABLE 1. AM1 results for 1-chlorosilatrane: fully optimized geometries as a function of Si–N distance (approximate C_3 symmetry)

Bond length (Si–N) (pm)	Heat of formation (kcal mol^{-1})	Average angle [a] (°)	Dipole moment (D)	Atomic charge on silicon	Atomic charge on nitrogen	Bond order (Si–N)	*E*(Si–N) (eV)	*E*(Si–Cl) (eV)
200.0	−220.27	−16.8	10.42	1.503	−0.266	0.326	−7.31	−10.91
220.0	−226.16	−7.0	9.42	1.516	−0.282	0.244	−6.07	−11.90
240.0	−230.81	0.3	8.08	1.524	−0.309	0.169	−5.14	−11.26
257.9	−232.29	5.6	6.90	1.524	−0.342	0.114	−4.46	−11.35
260.0	−232.28	5.8	6.78	1.524	−0.348	0.108	−4.39	−11.35
280.0	−230.95	9.2	5.51	1.517	−0.390	0.063	−3.71	−11.39
300.0	−229.87	8.4	4.34	1.506	−0.405	0.033	−2.98	−11.40
320.0	−230.46	9.0	3.33	1.500	−0.368	0.016	−2.20	−11.42
333.8	−230.89	8.5	2.66	1.497	−0.321			
340.0	−230.75	8.2	2.39	1.498	−0.305	0.007	−1.55	−11.45
360.0	−227.76	7.8	1.51					

[a] Average of the three O–Si–N–C dihedral angles around the Si–N bond.

1-fluorosilatrane (253.2 pm and 331.0 pm respectively) [1]. This result contradicts the XD results, but it should be noted that the energy surface is flat around the minima and an energy of only 0.01 kcal mol^{-1} is required to shorten the Si–N distance by 2 pm. The average of the three O–Si–N–C dihedral angles is suitable for describing the conformation of the whole skeleton. As the Si–N distance is shortening, this angle becomes more negative; at long distances it remains constant and positive (Table 1). The same tendency was found in other silatranes [1,2].

The value of dipole moment decreases as the Si–N bond lengthens. The atomic charge on silicon is calculated to be strongly positive and it has a very flat maximum at 260 pm, near to the optimum *endo* Si–N distance. The atomic charge on nitrogen is strongly negative, with a more important variation. It has a minimum at 300 pm and increases rapidly at longer distances. The positive atomic charge on silicon is 0.22 charge unit less than in 1-fluorosilatrane [1] and 0.08 charge unit less than in 1-methylsilatrane [2]; this effect is somewhat surprising and it may reflect the strong electron back donation from chlorine. There is no difference between the negative atomic charge on the nitrogen in the three molecules [1].

The Si–N bond order is large if the Si–N distance is less than 260 pm. At longer distances (above 280 pm) it is halved for each increase of 20 pm. This behaviour may be compared with the non-bonding distance proposed by Glidewell [12] and it is independent of substituent [1,2].

The energy partitioning shows a rather strong Si–N interaction even at large distances. A detailed analysis shows that the energy contribution of the resonance term decreased rapidly, but the sum of the electrostatic terms was high even at large Si–N distances because of the high negative charge on the nitrogen. In the *endo* form the resonance term was equal to −1.49 eV. The opposite energy behaviour of the two axial bonds (Si–N and Si–Cl) is in agreement with other AM1 and *ab initio* results for similar compounds [1,19,21] and it supports the leaving group theory. Moreover, while the energy partitioned to the Si–N bond does not show large variations in the *endo* equilibrium as the substituent change (−5.03 eV, −4.43 eV and −4.46 eV in the F, Me and Cl derivatives), the leaving group property of chlorine is clearly reflected in the Si–X energies (−19.63 eV, −16.78 eV and −11.35 eV in the F, Me and Cl derivatives).

The Si–N distance of the *endo* form is predicted by the AM1 method to be 15 pm longer than the HF/6-31G(d) optimum [22]. If this overestimation is transferable, the HF/6-31G(d) Si–N distance of the *endo* form is predicted to be about 243 pm. This value may be compared with the future ED results. The energy hypersurface is very flat around the two minima. There is a very small (a few kilocalories per mole) energy barrier between the two local minima at 300 pm, and the *exo* form is the more stable. These results suggest that the *endo* form may be easily transformed into the *exo* form and *vice versa*. Only a small amount of energy is required to change the Si–N distance between 240 and 340 pm. These results agree with the earlier results [1,2].

The calculated AM1 zero-point energy in the *endo* minimum is 123.2 kcal mol^{-1} and in the *exo* minimum it is 123.7 kcal mol^{-1}. The frequency analysis shows that no pure Si–N vibrational frequency exists.

In order to test the flexibility of the ethoxy links a series of geometry optimizations was made with one of the links forced out of C_3 symmetry (Table 2) as was defined in the earlier papers [1,2]. When the Si–N distance is 200 pm, this conformation does not exist as a different energy minimum. It appears above 220 pm in a separate energy valley with a single local minimum at 260.0 pm. At longer Si–N distances the symmetrical form becomes increasingly advantageous energetically, and it is easier to "pull out" the nitrogen atom if the

TABLE 2. AM1 results for 1-chlorosilatrane: fully optimized geometries as a function of Si–N distance (no symmetry assumed)

Bond length (Si–N) (pm)	Heat of formation (kcal mol^{-1})	Dipole moment (D)	Atomic charge on silicon	Atomic charge on nitrogen	Bond order (Si–N)	*E*(Si–N) (eV)	*E*(Si–Cl) (eV)
220	−225.12	9.45	1.514	−0.278	0.245	−6.04	−11.08
240	−229.90	8.17	1.529	−0.307	0.169	−5.13	−11.27
260	−230.93	6.96	1.538	−0.345	0.109	−4.42	−11.40
280	−228.68	5.86	1.538	−0.385	0.065	−3.76	−11.46
300	−226.38	4.86	1.532	−0.399	0.035	−3.04	−11.48
320	−225.16	3.93	1.529	−0.362		−2.23	−11.50
340	−223.41	3.17	1.534	−0.299		−1.57	−11.55

TABLE 3. AM1 results for 1-chlorosilatrane: fully optimized geometries as a function of O–Si–N–C dihedral angle (approximate C_3 symmetry)

Average dihedral angle [a] (°)	Heat of formation (kcal mol^{-1})	Bond length (Si–N) (pm)	Dipole moment (D)	Atomic charge on silicon	Atomic charge on nitrogen	Bond order (Si–N)	E(Si–N) (eV)	E(Si–Cl) (eV)
−20	−228.59	246.9	7.57	1.563	−0.331	0.146	−4.97	−11.43
−10	−230.74	250.7	7.49	1.550	−0.334	0.135	−4.81	−11.40
0	−232.09	255.5	7.14	1.533	−0.339	0.120	−4.58	−11.37
10	−232.12	259.6	6.71	1.516	−0.345	0.109	−4.38	−11.33
20	−230.58	260.8	6.31	1.504	−0.346	0.105	−4.28	−11.30

[a] Average of the three O–Si–N–C dihedral angles around the Si–N bond.

links are symmetrically ordered. The second (*exo*) local energy minimum does not exist in the asymmetric conformation.

The energy barrier to restore an ethoxy link that is out of symmetry back to the symmetrical position has been found to be small (about 1 kcal mol^{-1}) at an Si–N distance of 260 pm in agreement with earlier results [1,2]. The small amount of energy required to make one of the ethoxy links planar supports the existence of disordered structures in crystal phase [6] and is in accordance with NMR observations which indicate that the silatrane skeleton is flexible [13].

The dihedral angles calculated by the AM1 method do not agree with the solid-phase results. The dihedral angles are not given explicitly in the original paper; they were calculated from the crystal coordinates after correcting the misprinted y coordinate of the C_3 atom [10]. The conformation of the whole silatrane skeleton may be represented by the O–Si–N–C and the C–O–Si–N dihedral angles. In the solid-state experimental geometry the C–O–Si–N angles are between −3.8° and −4.3° and the O–Si–N–C angles are between −8.7° and −9.7°. In the AM1 (C_3, *endo*) geometry the C–O–Si–N angle is −33.0° and the O–Si–N–C angle is 5.6°. If the Si–N distance is fixed at 220 pm, the two equilibrium dihedral angles are −15.3° and −7.0° respectively; at 200 pm they are −1.0° and −16.8°. In contrast with earlier results [1,2] it is not possible to find an Si–N distance where the calculated and experimental dihedral angles agree well. It should be noted that the origins of this disagreement are the relatively small dihedral angles in the XD geometry of 1-chlorosilatrane compared with other experimental geometries [6–9]. The calculated and the measured dihedral angles agree best for an Si–N distance somewhere between 200 and 220 pm, near to the experimental Si–N distance.

Further studies show that the energy requirement for rotating the O–Si–N–C dihedral angle by −10° is only 0.8 kcal mol^{-1}, and this shortens the Si–N distance by 4.8 pm (Table 3). The average of the three C–O–Si–N dihedral angles was changed to −14°. The Si–N bond order also increases in step with the Si–N and Si–Cl diatomic energy contribution. In this case the strength of both axial bonds (Si–N and Si–Cl) increases as both bonds become shorter.

TABLE 4. PM3 results for 1-chlorosilatrane: fully optimized geometries as a function of Si–N distance (approximate C_3 symmetry)

Bond length (Si–N) (pm)	Heat of formation (kcal mol^{-1})	Average angle [a] (°)	Dipole moment (D)	Atomic charge on silicon	Atomic charge on nitrogen	Bond order (Si–N)	E(Si–N) (eV)	E(Si–Cl) (eV)
200.0	−252.83	−16.4	9.98	1.069	0.130	0.375	−4.46	−9.63
220.0	−255.39	−5.4	8.98	1.098	0.065	0.277	−3.37	−9.87
240.0	−257.09	0.5	7.73	1.124	−0.004	0.185	−2.53	−10.12
245.5	−257.23	0.4	7.38	1.130	−0.022	0.163	−2.35	−10.17
260.0	−256.39	2.2	6.51	1.142	−0.068	0.113	−1.92	−10.29
280.0	−253.88	3.0	5.39	1.151	−0.129	0.064	−1.41	−10.38
300.0	−253.97	1.7	4.28	1.157	−0.127	0.028	−0.72	−10.40
318.9	−255.00	−7.8	3.38	1.161	−0.102			
320.0	−254.94	−7.7	3.34	1.161	−0.101	0.011	−0.31	−10.50
340.0	−252.97	−5.4	2.44	1.165	−0.082	0.005	−0.14	−10.58

[a] Average of the three O–Si–N–C dihedral angles around the Si–N bond.

TABLE 5. PM3 results for 1-chlorosilatrane: fully optimized geometries as a function of Si–N distance (no symmetry assumed)

Bond length (Si–N) (pm)	Heat of formation (kcal mol^{-1})	Dipole moment (D)	Atomic charge on silicon	Atomic charge on nitrogen	Bond order (Si–N)	*E*(Si–N) (eV)	*E*(Si–Cl) (eV)
200	−252.52	10.23	1.098	0.065	0.377	−4.48	−9.54
220	−255.09	9.01	1.100	0.068	0.277	−3.36	−9.87
240	−256.61	7.78	1.125	−0.001	0.185	−2.52	−10.12
260	−255.44	6.59	1.144	−0.063	0.113	−1.90	−10.31
280	−252.99	5.51	1.152	−0.127	0.064	−1.39	−10.39
300	−252.59	4.46	1.159	−0.123	0.029	−0.71	−10.42
320	−252.25	3.60	1.166	−0.096	0.011	−0.33	−10.50
340	−248.84	2.83	1.171	−0.075	0.005	−0.13	−10.59

Three findings can be drawn from these results.

(a) The geometry found in the crystal structure is a preferred position for both the Si–N and the Si–Cl bonds.

(b) As the nitrogen is pushed towards the silicon, the torsional angle of the skeleton is changed. There is a stretching torsion interaction in the silatrane skeleton for the Si–N bond. No pure Si–N stretching frequencies are expected in the IR spectra.

(c) The Si–N distance is closer to the solid-phase result; the calculated dihedral angles are closer to the experimental values. However, the disagreement remains considerable.

Table 4 lists the PM3 heats of formation, dipoles and other important calculated values for 1-chlorosilatrane which can be compared directly with the AM1 results in Table 1. The heat of formation again shows two minima as a function of the Si–N distance. The equilibrium Si–N distances (*endo* and *exo*) are 12.4 and 14.9 pm shorter than the corresponding AM1 distances. The *endo* structure is more stable by 2.2 kcal mol^{-1}. The PM3 parametrization gives always a shorter Si–N equilibrium distance than the AM1 [1,2], but this bond shortening is the largest in the case of 1-chlorosilatrane. The *endo* Si–N distance is 4.7 pm shorter than the corresponding PM3 value in the 1-fluorosilatrane (250.2 pm) [1]. This result agrees with the tendencies found in the XD structures, but it contradicts the AM1 results. The energy surface is flat around both minima, *e.g* the 5.5 pm Si–N distance shortening in the *endo* conformer causes a change in the energy of only 0.14 kcal mol^{-1}. The energy barrier is located between 280 and 300 pm. The results are quantitatively different from the AM1 results but they lead to similar conclusions.

The average of the three O–Si–N–C dihedral angles around the Si–N bond (Table 4) agrees well with the dihedral angles obtained by the AM1 method (Table 1) below 260 pm, but there is considerable disagreement above 300 pm. This different conformation stabilizes the PM3 geometry at longer Si–N distances. The PM3 dipole moments and atomic charges are considerably less than the AM1 values (Table 1).

The atomic charge on silicon (Table 4) is strongly positive, but much less than the AM1 atomic charge. The charge on the silicon increases as the Si–N distance increases. The calculated positive charge on silicon agrees well with the charge calculated in the case of 1-fluorosilatrane [1], and it is 0.16 charge unit more than in the case of 1-methylsilatrane [2]. The atomic charge on nitrogen is slightly positive at shorter Si–N distances (below 240 pm) and at longer distances it is slightly negative. This is one of the most important differences between the PM3 and AM1 results and it is reflected in the differences in the other calculated properties (dipole moments and energy partitioning).

TABLE 6. PM3 results for 1-chlorosilatrane: fully optimized geometries as a function of O–Si–N–C dihedral angle (approximate C_3 symmetry)

Average dihedral angle [a] (°)	Heat of formation (kcal mol^{-1})	Bond length (Si–N) (pm)	Dipole moment (D)	Atomic charge on silicon	Atomic charge on nitrogen	Bond order (Si–N)	*E*(Si–N) (eV)	*E*(Si–Cl) (eV)
−20	−254.07	231.8	8.02	1.123	0.020	0.221	−2.83	−10.12
−10	−256.28	239.4	7.73	1.126	−0.006	0.189	−2.57	−10.16
0	−257.23	245.1	7.41	1.130	−0.021	0.164	−2.36	−10.17
10	−256.54	246.3	7.24	1.131	−0.017	0.159	−2.28	−10.16
20	−254.73	242.7	7.23	1.128	−0.002	0.171	−2.36	−10.13

[a] Average of the three O–Si–N–C dihedral angles around the Si–N bond.

TABLE 7. Comparison of the calculated energy differences and energy barriers in the substituted silatranes

Substituent	*E*(*exo* – *endo*) (kcal mol^{-1})		*E*(barrier – *endo*) (kcal mol^{-1})	
	AM1	PM3	AM1	PM3
Cl	1.4	2.2	2.5	3.4
F	3.0	0.4	3.5	2.4
Me	–1.0	–1.8	1.3	1.4

The same kind of difference was found in the case of 1-fluorosilatrane [1] and 1-methylsilatrane [2] between AM1 and PM3 parametrizations.

The calculated Si–N bond orders are larger than those calculated by AM1 method, but they show the same tendency. The energy partitioning shows that the Si–N interaction starts to diminish quickly above 280 pm. The absolute values are much smaller than those calculated by AM1. A detailed analysis shows that the energy contributions of the resonance term are almost the same in the two different methods. The origin of the difference is the electrostatic term. The electrostatic contribution in the *endo* form is small, –0.26 eV, for the PM3 parametrization while it is –3.10 eV for the AM1 method. This difference can be explained by the much smaller calculated charge on the nitrogen by the PM3 parametrization. The Si–N bond is predicted to be stronger and less polar. The leaving group properties of chlorine are quite well represented in this parameterization too.

Further geometry parameters are given in Figs. 1 and 2. The Si–O distances calculated by the PM3 parametrization are shorter and the C–N distances are longer than the corresponding distances calculated by the AM1 method, and they agree usually better with the experiments [1,2,6–9]. However, in the experimental geometry of the 1-chlorosilatrane, some deviations can be found in the ethoxy links. The very short C–C and C–N distances (143 and 144 pm) and the unusually planar links are not justified by the calculations and by other experimental results. These facts signal that the measured XD geometry may be an average of disordered ring structures. The C–H distances calculated by the PM3 parametrization are shorter and also more

TABLE 8. Experimental (X-ray diffraction and electron diffraction) and fully optimized geometrical parameters calculated by AM1 and PM3 parametrizations for 1-chloro-, fluoro-, methyl- and hydroxy-substituted silatranes

Parameter (units)	Method of parameter determination	Value for the following substituents			
		Cl	F	Me	OH [22]
Si–N bond length	(pm) AM1	257.9	253.2	260.3	252.7
	(pm) PM3	245.5	250.2	256.3	
	(pm) ED		232.4	245.3	
	(pm) XD	202.3	204.2	217.5	
Si–O bond length	(pm) AM1	176.6	176.2	177.4	176.3
	(pm) PM3	170.4	170.9	171.3	
	(pm) ED		165.2	165.6	
	(pm) XD [a]	164.9	164.5	167.0 [b]	
C–N bond length	(pm) AM1	144.8	144.9	144.6	144.9
	(pm) PM3	148.6	148.4	148.1	
	(pm) ED		148.1	145.8 [c]	
	(pm) XD [a]	144.9 [c]	147.0	147.7	
C–C bond length	(pm) AM1	154.8	154.9	154.7	
	(pm) PM3	154.5	154.8	154.3	
	(pm) ED		151.4	155.8	
	(pm) XD [a]	143.4 [c]	146.4 [c]	152.6	

The AM1 and PM3 data are from the present work and from refs. 1 and 2, and the experimental values are from refs. 6–10.

[a] The average of three bond lengths.

[b] There are two longer bonds (167.3 and 168.0 pm) among the three.

[c] Probably too short distances.

realistic. The N–Si–Cl angle was always very close to 180°.

The calculated PM3 zero-point energy of the *endo* geometry is 116.9 kcal mol^{-1}. The frequency analysis shows a combined Cl–Si–N vibration at 364 cm^{-1} in the *endo* form.

Table 5 lists the results calculated by PM3 method. The asymmetric form has a single minimum at a shorter Si–N distance (*endo* form). The energy function is always higher than the energy function of the symmetric form and it is extremely flat between 280 and 320 pm. The calculated values show the same tendencies observed in Tables 2 and 4. The dipole moment, the absolute values of atomic charges and the diatomic energy contributions are systematically smaller in the PM3 parametrization than in the AM1 method.

Table 6 lists the PM3 results obtained by rotating the O–Si–C–N dihedral angle. There is a qualitative agreement between the PM3 and AM1 results in Table 3. The energy required to rotate the O–Si–C–N angle by −10° is 1 kcal mol^{-1} and it shortens the Si–N distance by 5.7 pm (Table 6). The average of the three C–O–Si–N dihedral angles changed to −15°. The Si–N bond order increased, parallel to the Si–N diatomic energy contribution. The energy required to rotate the O–Si–C–N angle by −20° is 3.2 kcal mol^{-1}. The rotation in the opposite direction requires an even smaller energy (in agreement with AM1 results) and causes Si–N bond shortening (disagreement with AM1 results). The other calculated values show the characteristic differences between the PM3 and AM1 parametrizations. However, there is considerable agreement between the tendencies of the two parametrizations which therefore seem to be model independent. The most important findings based on the AM1 results are supported by the PM3 results (Table 7). However, in the case of 1-chlorosilatrane there is disagreement between the two methods in respect of the Si–N distance. According to the PM3 results the shortest Si–N distance is expected in the case of 1-chlorosilatrane in agreement with the XD results [10]; the AM1 method predicts the shortest Si–N distance to occur in the case of 1-fluorosilatrane (Table 8).

Table 8 lists several calculated and measured geometrical parameters. The following findings can be drawn from the data.

(1) The bond lengths in the ethoxy links are quite independent of experimental methods and substituents. The different semiempirical parametrizations show systematic errors which are again independent of substituents.

(2) The AM1 parametrization systematically overestimates the Si–O bond lengths by 10–12 pm.

(3) The PM3 parametrization systematically overestimates the Si–O bond lengths by 4–6 pm.

(4) The AM1 parametrization systematically underestimates the C–N bond lengths by 3–4 pm while the PM3 parametrization gives good results.

(5) The C–C bond lengths are predicted quite consistently by the two semiempirical methods.

(6) The measured C–C bond lengths in the 1-chlorosilatrane are too short: they are even shorter than in the 1-fluorosilatrane in which the carbon atoms linked to nitrogen are disordered [6].

If all these facts are considered—together with the small dihedral angles of the ethoxy links in the 1-chlorosilatrane—it is probable that the XD structure of the 1-chlorosilatrane is disordered too.

4. Conclusions

The main findings of this paper are as follows.

(1) Two minima were found by both semiempirical methods on the energy profile when C_3 symmetry was retained with two different Si–N distances (*endo*-C_3 and *exo*-C_3 forms).

(2) There exists a third asymmetrical conformation in a separate minimum in which the Si–N distance is nearly identical with the Si–N distance found in the *endo*-C_3 conformation.

(3) The *endo* Si–N distance calculated by the PM3 parametrization is shorter than the corresponding distance calculated in the 1-fluorosilatrane in agreement with the experimental observation and in contradiction with the AM1 results.

(4) The AM1 and PM3 methods show systematic errors in calculating the Si–O bond length. The PM3 results are much closer to the experimental results.

(5) The energy cost of shortening the Si–N distance has been found to be small; the energy hypersurface is rather flat, with the silatrane skeleton being flexible. The calculations show that the crystal forces could easily distort the gas-phase structure.

(6) Comparison of the published XD structure of the 1-chlorosilatrane with the calculated geometry and with the other experimental geometries of other silatranes leads to the conclusion that the ethoxy links should be disordered.

(7) The Si–N distance has been found to depend on the O–Si–N–C dihedral angle; turning this angle closer to the crystal phase results in a decrease in the equilibrium Si–N distance. The energy required to turn this dihedral angle by 20° is a few kilocalories per mole.

(8) The calculated Si–N bond orders and energy partitioning show an existing Si–N bond at distances below 260–270 pm.

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