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MNDO, AM1 and PM3 semiempirical molecular orbital study of 1-fluorosilatrane *

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Abstract

MNDO, AM1 and PM3 semiempirical models have been employed to study the bonding and structure of 1-fluorosilatrane using full geometry optimization. Heats of formations were calculated at different Si–N distances between 200 pm and 360 pm. Two minima were found on the energy profile when C_3 symmetry was retained. A third local energy minimum has been found, in a non-symmetrical conformation.

1. Introduction

Silatranes ($RSi(OCH_2CH_2)_3N$, 1-organyl-2,8,9-trioxa5-aza-1-silatricyclo [3.3.3.$0^{1.5}$] undecanes) are biologically active, silicon-containing organic molecules (Fig. 1) [1–4]. The most important structural feature of these molecules is the transannular Si–N donor–acceptor bond. Two forms of the structure may be proposed. In the *endo* form the central silicon is bonded to a nitrogen through three ethoxy bridges and *vi* a dative bond. The lone pair of the nitrogen turns toward the silicon and the Si–N distance is relatively short (Fig. 1). In the *exo* form the nitrogen lone pair is outside, and the resulting Si–N distance is much longer (Fig. 2).

In crystalline samples of many substituted silatranes short Si–N distances have been observed, so the *endo* form is known to exist in the solid state. Gas-phase electron diffraction (ED) measurements show longer Si–N distances in 1-fluorosilatrane: 204.2 pm (X-ray) [5], 232.4 pm (ED) [6], and in 1-methylsilatrane: 217.5 pm (X-ray) [7], 245 pm (ED) [8]. In 1-chlorosilatrane the Si–N distance is 202.3 pm (X-ray) [9]; 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 pm or 189.5 pm) [10,11], but shorter than the sum of the appropriate non-bonded radii (269 pm) [11] and much shorter than the sum of van der Waals radii (350 pm) [10]. The Si–N distance is also variable in solution, shortening in polar solvents and lengthening in non-polar solvents [8]. The Si–N distance have been found to depend on the nature of substituent R. If electron-withdrawing, the substituent (R = fluorine or chlorine) shortens the Si–N distance by decreasing the electron density on silicon and thus increasing its electron acceptor potential leading to a stronger Si–N dative bond.

This is in agreement with the experimental results. Methyl substitution has an opposite effect, resulting in a longer Si–N bond. The bond lengthening is found to be about 13 pm in both types of measurement.

The silatrane skeleton has been found to have approximately C_3 symmetry in the solid state. This symmetry is only approximate because of the high flexibility of the ethoxy links between silicon and nitrogen [5,7,9]. A partially disordered structure has been found in 1-fluorosilatrane. The average distance of disordered atoms from a symmetry plane is 47 pm [5], which shows very marked flexibility. NMR data also show very fast ring inversions in solution [12] for other substituted silatranes. The existence of different polymorphic modifications had been explained by freezing of intramolecular movements.

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* Dedicated to Professor M.G. Voronkov in recognition of his important contributions to organosilicon chemistry.

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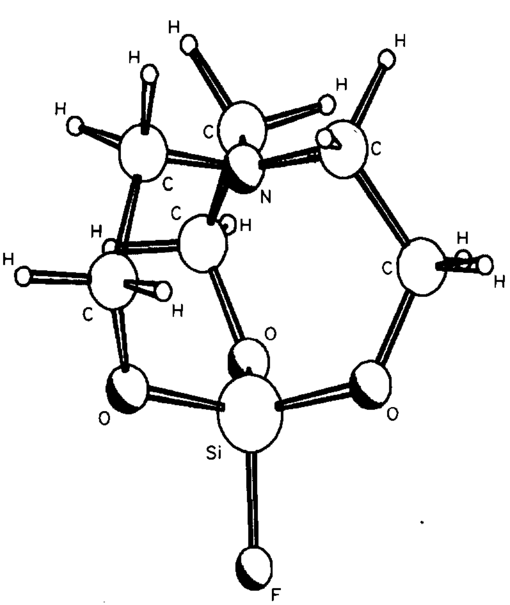

Fig. 1. Molecular diagram with labelling scheme for *endo*-C_3 form of 1-fluorosilatrane (AM1 equilibrium geometry).

The high dipole moments of silatranes may influence their biological activity by facilitating penetration of membranes [1].

Early theoretical investigations of silatranes were limited by the size of the molecule, its conformational flexibility, the lack of experimental geometries and the limited methods then available for geometry optimization and computation. By 1975 only seven experimental geometries of silatranes had been reported in the literature. Nowadays this number is approaching one hundred. In early theoretical papers the CNDO/2 hamiltonian was mostly applied. Calculations showed that the *endo* form is preferred to the *exo* form, and the Si–N bonding energy was found to be between 0.70 and 1.09 eV and the Si–N Wiberg indices between 0.33 and 0.46. Calculations were performed without geometry optimization, and the geometries were usually taken from X-ray experiments. 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 [1], the importance of d orbitals was questioned and another, so-called hypervalent model was proposed [13].

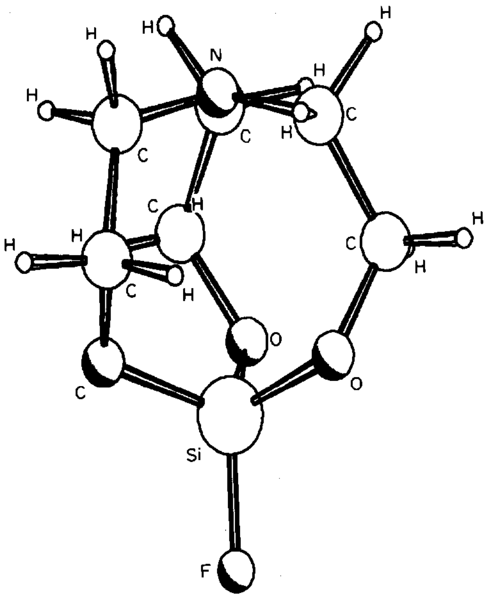

Fig. 2. Molecular diagram with labelling scheme for *exo*-C_3 form of 1-fluorosilatrane (AM1 equilibrium geometry).

The *ab initio* theory was also applied, but no geometry optimizations were performed. Only simple model compounds of neutral pentacoordinated adducts were calculated with full geometry optimization. The predicted stabilization energy of the NH_3–SiF_4 adduct was calculated to be 10.0 and 8.6 kcal/mole respectively with minimal and double zeta bases set [14,15]. The existence of NH_3–SiF_4 adduct was experimentally demonstrated [16]. A number of *ab initio* calculations show the existence and stability of neutral pentacoordinated compounds containing a silicon–nitrogen bond [17–19]. 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 [19].

Gordon *et al.* [20] used the AM1 semiempirical method fully to optimize 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 also optimized at the 6 – 31(d) *ab initio* level. This permitted direct comparison of *ab initio* and AM1 optimized 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 compared to the *ab initio* results, but the general trends are well reproduced. Utilizing the Bader electron density analysis [21], it was found that the Si–N bond critical point still exists at larger Si–N distances, and only 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.* [22] studied 1-methylsilatrane and model compounds by HF/3–21G(d) *ab initio* theory. No geometry optimization was performed, and the calculations were done in two points, with solid state and approximate gas phase geometry being applied. It was found that the Mulliken charges do not change much as the Si–N distance is varied, the silicon remaining strongly positive and the nitrogen strongly negative.

Calculations for 1-fluorosilatrane are included in the present study. Three recent semiempirical model hamiltonians were used in order to study the effects of parametrization, their utility and limitations. MM2 force field calculations were also performed in order to study the performance of a force field method in a difficult situation and to get a quick insight into the molecular structure.

2. Computational methods

All geometries were fully optimized with the semiempirical MNDO [23], AM1 [24] and PM3 [25] methods using adapted versions of the MOPACK [26] program. The MM2 force field was also applied [27]. The calculations were carried out on an i486/33MHz workstation and on an IBM RS/6000 model 320H. A self written graphics program was used to facilitate geometrical analysis of the structures.

No symmetry constraints were imposed during the geometry optimizations and the precise keyword of MOPACK was used throughout. A C_3-like and a completely nonsymmetric geometry were optimized separately. The Si–N distance was varied between 200 and 360 pm in steps of 20 pm, and the 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. 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 linking the silicon and nitrogen. Mulliken charges, dipole moments, bond orders and energy partitioning were also calculated.

3. Results and discussion

The MM2 force field is not expected to be able to describe pentacoordinated silicon bonding without serious modifications. The Si–N interaction is virtually non existent in that model. However in a short preliminary study two minima were found (*endo* and *exo*) with an energy barrier between them. The *exo* form was found to be much more stable.

The AM1 heats of formation, dipoles and other important calculated values are listed in Table 1 for 1-fluorosilatrane. The geometry has approximate C_3 symmetry (Figs. 1 and 2). The latest available parameters for silicon were used [28] in the calculations. The function of the heat of formation shows two minima. The shorter equilibrium Si–N distance is 253.2 pm in the *endo* form and the longer is 331.0 pm in the *exo* form. The dipole moment decreases with lengthening of the Si–N bond. The slope of the dipole moment function is steepest between 220 and 280 pm, where its value is about −0.05 Debye/pm.

The atomic charge on silicon is calculated to be strongly positive and it has a very flat maximum (+1.742) at 260 pm, near to the optimum *endo* Si–N distance. The atomic charge on nitrogen remains strongly negative, with more variation and maximum of −0.408 at around 300 pm. It decreases sharply at greater distances. The existence of the strongly positive Si and the strongly negative N agrees with *ab initio*

TABLE 1. AM1 results for 1-fluorosilatrane, fully optimized geometries as a function of Si–N distance [a]

Bond length (Si–N) (pm)	Heat of formations (kcal)	Average dihedral angle [b] (Si–N) (°)	Dipole (D)	Atomic charge on silicon	Atomic charge on nitrogen	Bond order Si–N	*E*(Si–N) (eV)	*E*(Si–F) (eV)
200.0	−277.10	−16.1	9.37	1.696	−0.280	0.316	−7.68	−19.24
220.0	−282.35	−8.0	8.39	1.716	−0.296	0.231	−6.43	−19.41
240.0	−286.22	−3.0	7.26	1.733	−0.325	0.154	−5.52	−19.56
→ 253.2	−287.09	0.2	6.47	1.741	−0.348	0.114	−5.03	−19.63
260.0	−286.92	1.8	6.07	1.742	−0.361	0.095	−4.80	−19.65
280.0	−284.98	6.6	4.86	1.737	−0.400	0.054	−4.13	−19.66
300.0	−283.51	8.0	3.79	1.731	−0.408	0.027	−3.36	−19.66
320.0	−283.81	7.7	2.83	1.728	−0.364	0.012	−2.50	−19.68
→ 331.0	−284.05	7.3	2.35	1.729	−0.329			
340.0	−283.78	7.1	1.97	1.731	−0.300	0.005	−1.76	−19.72
360.0	−280.41	6.8	1.18	1.737	−0.238			−19.76

[a] Note: approximate C_3 symmetry was held. [b] Average of the three O–Si–N–C dihedral angles around the Si–N bond.

3-21G(d) Mulliken charges [21]. It should be noted that the HF/3-21G(d) calculations have a tendency to give high charges.

The Si–N bond order is large if the Si–N distance is less than 260 pm. At longer distances it is halved for each increase of 20 pm. This behaviour may be compared to the non bonding distance proposed by Glidewell [11].

The energy partitioning shows a strong Si–N bond even at long distances. A detailed analysis shows that the energy contribution of the resonance term, which is responsible for bonding, decreases rapidly, but the sum of the three electrostatic terms (core–core, electron–core and electron–electron) remains very high at long Si–N distances and goes through a maximum (−3.45 eV) at a Si–N distance of 280 pm. This may be explained by the high and increasing negative charge on the nitrogen as the Si–N distance increases to 300 pm. The energy contribution of the Si–F bond increases monotonically as the Si–F distance shortens. The opposite behaviour of the two axial bonds is in agreement with *ab initio* results [18,20].

Several other geometric parameters change monotonically. The values given here are the values calculated at 200, 253.2 and 331 pm Si–N distances. The Si–F bond distances are 160.3, 160.0 and 159.6 pm, the average Si–O distances are 179.1, 176.2 and 175.1 pm and the O–Si–N bond angles are 88.1°, 78.4° and 68.6° respectively. The Si–O distances are usually overestimated by the AM1 method [20]. In this case they are 10–14 pm longer than the solid state values [5]. The N–Si–F angle was always 180°.

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 [20]. If this overestimation is transferable, the gas phase Si–N distance of the *endo* form is predicted to be about 238 pm. This value may be compared with the observed distance of 232.4 pm (ED) [6]. It is important to note that the energy hypersurface is very flat. A shortening by 13 pm of the Si–N distance from the equilibrium requires only 0.9 kcal/mole, and 5 kcal/mole is required to shorten the Si–N distance by 33 pm. This agrees with earlier results for the 1-hydroxysilatrane [20]. The energy difference between the two local minima is 3 kcal/mole and there is an energy barrier at 300 pm. The energy surface is extremely flat around the second minimum; less than 0.5 kcal/mole is required to shorten the Si–N distance by 31 pm. These results suggest that the *exo* form of 1-fluorosilatrane may be easily transformed into the *endo* form, and only a little energy is required to change the Si–N distance.

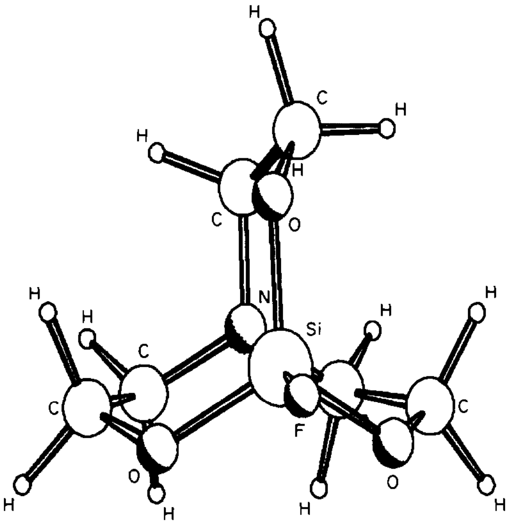

Fig. 3. Molecular diagram with labelling scheme for non-symmetric *endo* form of 1-fluorosilatrane (AM1 equilibrium geometry).

The calculated AM1 zero point energy of the geometry in the absolute minimum is 124.3 kcal/mole. The frequency analysis shows that no separate Si–N vibrational frequency exists.

It is suggested that the ethoxy links are very flexible. In order to study this flexibility another series of geometry optimizations was made, with one of the links forced out of the C_3 symmetry position (Fig. 3). When

TABLE 2. AM1 results for 1-fluorosilatrane, fully optimized geometry as a function of Si–N distance [a]

Bond length (Si–N) (pm)	Heat of formation (kcal)	Dipole (D)	Atomic charge on silicon	Atomic charge on nitrogen	Bond order (Si–N)	*E*(Si–N) (eV)	*E*(Si–F) (eV)
220.0	−281.32	8.39	1.726	−0.293	0.231	−6.40	−19.39
240.0	−285.40	7.28	1.735	−0.321	0.154	−5.50	−19.57
260.0	−285.87	6.22	1.750	−0.359	0.097	−4.80	−19.69
280.0	−283.15	5.22	1.758	−0.396	0.056	−4.14	−19.77
300.0	−280.37	4.32	1.755	−0.405	0.029	−3.37	−19.78
320.0	−278.96	3.51	1.757	−0.358	0.014	−2.48	−19.81
340.0	−276.91	2.84	1.765	−0.293	0.007	−1.75	−19.85

[a] No symmetry was supposed.

TABLE 3. AM1 results for 1-fluorosilatrane, fully optimized geometry as a function of O–Si–N–C dihedral angle [a]

Average dihedral angle [b] (Si–N) (°)	Heat of formation (kcal)	Bond length (Si–N) (pm)	Dipole (D)	Atomic charge on silicon	Atomic charge on nitrogen	Bond order (Si–N)	*E*(Si–N) (eV)	*E*(Si–F) (eV)
−20	−284.37	245.1	6.95	1.763	−0.344	0.139	−5.44	−19.74
−10	−286.27	247.9	690	1.752	−0.344	0.128	−5.27	−19.70
0	−287.08	252.8	6.51	1.741	−0.349	0.115	−5.06	−19.63
10	−286.50	256.8	6.00	1.726	−0.352	0.102	−4.85	−19.55
20	−284.47	259.0	5.54	1.718	−0.355	0.101	−4.77	−19.48

[a] Approximate C_3 symmetry was held. [b] Average of the three O–Si–N–C dihedral angles around the Si–N bond.

the Si–N distance is 200 pm the non-symmetrical form does not exist as a different energy minimum. However at larger distances a separate energy minimum exists for the non-symmetrical form. The results are summarized in Table 2. The energy of the non-symmetrical form is always higher, but the difference is rather small at shorter Si–N distances (about 1 kcal/mole). At longer distances the symmetrical form is much more advantageous energetically, and it is easier to "pull out" the nitrogen when the links are symmetrically ordered. This is why only one energy minimum was found in the non-symmetrical form. The Si–N distances agrees well in the two different "*endo*" minima.

The energy barrier to restore an ethoxy link that is out of symmetry to the symmetrical position was calculated as 253.2 pm Si–N distance. The energy required to make planar this Si–O–C–C–N ring was 1.4 kcal/mole. This result supports the existence of disordered structures in the crystal phase [5] and is in accordance with NMR observations which indicate that the silatrane skeleton is highly flexible [12].

The dihedral angles calculated by the AM1 method do not agree with solid phase results. The conformation of the whole silatrane unit can be represented by the O–Si–N–C dihedral angle. The use of a second, dependent C–O–Si–N angle can be helpful too. In the solid state geometry the C–O–Si–N dihedral angle is 0° and the O–Si–N–C angle is −17° [7]. In the AM1 geometry the C–O–Si–N angle is −26° and the O–Si–N–C angle is 0°. However it was found that the energy requirement for rotating the O–Si–N–C dihedral angle by −20° is only 2.7 kcal/mole and this shortens the Si–N distance by 8 pm (Table 3). The Si–N bond order also increases in step with the Si–N diatomic energy contribution. It is interesting to note that in this case the strength of the Si–F bond increases with increasing strength of the Si–N bond, while both bonds become shorter.

Two 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 Si–F bonds, (b) as the nitrogen is pushed towards the silicon the torsional angles of the skeleton change. There is a stretching torsion interaction in the silatrane skeleton for the Si–N bond. No pure Si–N stretching frequencies can be expected in the IR spectra.

The MNDO, results does not differ markedly from the AM1 results, but they show a rather longer Si–N

TABLE 4. PM3 results for 1-fluorosilatrane, fully optimized geometries as a function of Si–N distance [a]

Bond length (Si–N) (pm)	Heat of formation (kcal)	Average dihedral angle [b] (Si–N) (°)	Dipole (D)	Atomic charge on silicon	Atomic charge on nitrogen	Bond order (Si–N)	*E*(Si–N) (eV)	*E*(Si–F) (eV)
200.0	−304.62	−13.2	8.10	1.073	0.136	0.357	−4.27	−13.88
220.0	−307.69	−6.5	7.13	1.101	0.069	0.259	−3.67	−14.03
240.0	−310.25	−1.2	6.04	1.128	−0.010	0.170	−2.38	−14.17
→ 250.2	−310.71	0.5	5.49	1.139	−0.035	0.103	−2.07	−14.23
260.0	−310.32	1.9	4.98	1.149	−0.065	0.111	−1.81	−14.29
280.0	−308.39	2.7	3.97	1.161	−0.127	0.057	−1.35	−14.37
300.0	−308.92	1.4	2.93	1.169	−0.127	0.025	−0.69	−14.41
320.0	−310.30	−7.8	2.16	1.182	−0.101	0.010	−0.31	−14.53
→ 320.7	−310.35	−7.7	2.13	1.182	−0.101			
340.0	−308.51	−5.5	1.41	1.192	−0.082	0.005	−0.14	−14.60

[a] Approximate C_3 symmetry was held. [b] Average of the three O–Si–N–C dihedral angles around the Si–N bond.

equilibrium distance (256 pm). Because of the known deficiency of the MNDO method in describing crowded molecules good results were not expected with that method, but in this case the MNDO and AM1 methods were comparable in performance. Detailed results are not given separately because of that similarity.

Table 4 lists the MNDO-PM3 results for the 1-fluorosilatrane, which can be compared directly with the AM1 results in Table 1. The function of the heat of formation shows two minima, similar to the AM1 results. The shorter equilibrium Si–N distance is 250.2 pm in the *endo* form and the longer is 320.7 pm in the *exo* form. These distances are somewhat shorter than the equilibrium Si–N distances given by the AM1 method, but because of the flat energy surface this difference is not so important. The main difference is in the shape of the energy surface. While the two minima given by the AM1 method are rather different in energy (the *endo* form is the preferred one), the energies given by the PM3 method are much closer to each other. The difference is only 0.36 kcal/mole, but the *endo* form remains lower in energy. Despite the differences in shape, the energy hypersurface is very flat, in agreement with the AM1 results. A shortening of 10 pm in the Si–N distance from the "*endo*" equilibrium only 0.5 kcal/mole energy. 6 kcal/mole is required to shorten the Si–N distance by 50 pm. The energy barrier of the Si–N bond lengthening is more than 2.3 kcal/mole and is located between 280 and 300 pm. The energy surface is flat around the "*exo*" minimum. About 2.0 kcal/mole is required to shorten the Si–N distance by 51 pm. These 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) at shorter distances (below 260 pm), but there is a considerable disagreement above 300 pm. This different conformation stabilizes the PM3 geometry when the Si–N distance is longer. The dipole moment decreases as the Si–N bond lengthens in a similar way to what was found with the AM1, but the predicted values are considerably less.

The atomic charge on silicon (Table 4) is strongly positive, but much less than the atomic charge calculated by the AM1 method. The charge on the silicon increases as the Si–N distance increases. The atomic charge on nitrogen is slightly positive at shorter Si–N distances (below 220 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, energy partitioning).

The calculated Si–N bond orders are larger than those calculated by the AM1 method, but they show the same tendency. The energy partitioning shows a Si–N bond even at large distances. The absolute values are much smaller than those calculated by AM1. A detailed analysis shows that the energy contribution of the resonance term is almost the same in the two different methods (the PM3 values are slightly higher). The origin of the difference is the sum of the three electrostatic terms. The electrostatic contribution is almost zero (−0.26 eV at 250.2 pm Si–N distance) with the PM3 method while it is 2.42 eV with the AM1 method. This difference can be explained by the much smaller calculated charge on the nitrogen, by the PM3 method. The energy contribution of the Si–F bond changes in the same way was in the case of AM1 method.

The values of the other geometric parameters which are given here are those calculated at Si–N distances of 200.0, 250.2 and 320.7 pm. The Si–F bond distances are 159.6, 158.8 and 157.8 pm, the average Si–O distances are 172.2, 170.9 and 169.8 pm and the O–Si–N bond angles are 88.0, 79.1 and 74.2 deg respectively. The Si–O distances calculated by the PM3 method are

TABLE 5. PM3 results for 1-fluorosilatrane, fully optimized geometry as a function of Si–N distance [a]

Bond length (Si–N) (pm)	Heat of formation (kcal)	Dipole (D)	Atomic charge on silicon	Atomic charge on nitrogen	Bond order (Si–N)	*E*(Si–N) (eV)	*E*(Si–F) (eV)
200	−304.00	8.17	1.071	0.142	0.359	−4.27	−13.83
220	−307.36	7.13	1.102	0.073	0.259	−3.16	−14.02
240	−309.78	6.10	1.130	0.030	0.170	−2.37	−14.17
260	−309.61	5.06	1.149	−0.066	0.103	−1.81	−14.29
280	−307.52	4.14	1.163	−0.125	0.057	−1.33	−14.37
300	−307.55	3.19	1.172	−0.123	0.025	−0.68	−14.43
320	−307.54	2.52	1.185	−0.096	0.012	−0.32	−14.53
340	−304.30	1.96	1.198	−0.075	0.005	−0.13	−14.60

[a] No symmetry was supposed.

TABLE 6. PM3 results for 1-fluorosilatrane, fully optimized geometry as a function of O–Si–N–C dihedral angle [a]

Average dihedral angle [b] (Si–N) (°)	Heat of formation H_f (kcal)	Bond length (Si–N) (pm)	Dipole (D)	Atomic charge on silicon	Atomic charge on nitrogen	Bond order (Si–N)	*E*(Si–N) (eV)	*E*(Si–F) (eV)
−20	−307.29	238.5	6.13	1.144	−0.001	0.179	−2.44	−14.29
−10	−309.62	244.8	5.88	1.142	−0.021	0.154	−2.25	−14.28
0	−310.67	250.3	5.51	1.139	−0.034	0.134	−2.08	−14.23
10	−309.98	251.3	5.25	1.137	−0.031	0.128	−1.99	−14.19
20	−308.09	248.3	5.15	1.133	−0.017	0.137	−2.04	−14.15

[a] Approximate C_3 symmetry was held. [b] Average of the three O–Si–N–C dihedral angles around the Si–N bond.

shorter than those calculated by the AM1 method, and they agree better with experimental data [5]. The N–Si–F angle was always 180 deg. The average C–H distance is 110 pm which is considerably shorter than the value calculated by AM1 (125 pm).

The calculated PM3 zero point energy of the "*endo*" geometry is 118.0 kcal/mole. The frequency analysis shows again that no separate Si–N vibrational frequency exists.

Table 5 lists the results calculated by PM3 method. The non-symmetric form has a single minimum at shorter Si–N distance. The most interesting property of the energy surface is that it is flat between 280 pm and 320 pm, and virtually no energy is required to change the Si–N distance in that range. 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 method than in the AM1 method. The difference is the most important in the case of atomic charge on the nitrogen.

The same kind of flexibility was found as earlier, with similar energy values. The energy barrier to restore an ethoxy link that is out of symmetry back into the symmetrical position is the energy required to make it planar (1 kcal/mole). The PM3 results do not differ essentially from the AM1 results in this respect, the ethoxy link is calculated to be even more flexible.

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–N–C dihedral angle by −20° is 3.4 kcal/mole and it shortens the Si–N distance by 12 pm (Table 4). The rotation in the opposite direction requires 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 parametrization. However there is a considerable agreement in tendencies among the two methods which therefore seem to be independent of model. The findings based on the AM1 results are supported by the PM3 results too.

4. Conclusions

The main findings of this paper are the following: Two minima was found on the energy profile when C_3 symmetry was retained by both semiempirical methods, with two different Si–N distances (*endo*-C_3 and *exo*-C_3 forms).

There exists a third, non-symmetrical conformation in a separate minimum in which the Si–N distance is nearly identical to the Si–N distance found in the *endo*-C_3 conformation.

The calculated *endo* Si–N distances are longer than the gas-phase experimental value by 18–21 pm. If the Si–N distance were corrected by a factor (−15 pm) originating from HF/6–31G(d) analogies, the predicted Si–N distance is close to the gas phase results.

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, with the equilibrium Si–N distance decreasing. The energy required to turn this dihedral angle by 20° is 2.7–3.4 kcal/mole.

The energy cost of shortening the Si–N distance has been found to be small, and 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 carbon atoms linking the nitrogen and oxygen must be disordered.

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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