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Conformational Analysis of *N*,*N*,*N*′,*N*′-Tetramethylsuccinamide: The Role of C−H···O Hydrogen Bonds

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We report a conformational analysis of *N*,*N*,*N*′,*N*′-tetramethylsuccinamide. An initial set of geometries was obtained through an exhaustive conformer search with molecular mechanics. The structures were further optimized using density functional theory (DFT) with the generalized-gradient approximation. Single-point energies on the DFT geometries are reported at the second-order Møller−Plesset (MP2) levels. The lowest energy conformations were further optimized at the MP2 level. Geometries and relative energies for 22 conformations are reported. The geometries are rationalized in terms of rotational potential energy surfaces in simple compounds, intramolecular C−H···O hydrogen bonding, and dipole−dipole repulsion.

Introduction

As part of our work on the ab initio design of ligands for effective and selective radionuclide complexation, we have been studying the structures of amides and their metal complexes.[1−5] Knowledge of the ligand geometry in the absence of the metal ion is an important prerequisite for understanding how these systems work. In prior studies, we reported the detailed conformational analyses of simple aliphatic amides,[3] malonamide, *N*,*N*′-dimethylmalonamide, and *N*,*N*,*N*′,*N*′-tetramethylmalonamide,[4] and *N*,*N*-dimethylformamide dimers.[5] The present study extends that work with an extensive conformational analysis of *N*,*N*,*N*′,*N*′-tetramethylsuccinamide, TMS (Scheme 1).

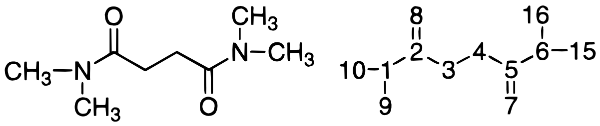
Previous calculations on succinamide conformations have been confined to *N*,*N*′-dimethylsuccinamide. Aleman and coworkers[6] reported three stable conformers for *N*,*N*′-dimethylsuccinamide at the Hartree−Fock level with the 6-31G* basis set. Single-point calculations including electron correlation effects at the MP2/6-31G* and MP3/6-31G* levels were then performed to calculate energies of these conformers. In this case, where N−H groups are present, intramolecular hydrogen bonds play a dominant role in stabilizing these structures. Similarly, intramolecular N−H···O hydrogen bonds stabilize the lowest energy forms of malonamide and *N*,*N*′-dimethylmalonamide.[4,7]

In the current study, we focus on TMS where intramolecular N−H···O hydrogen bonding is not possible. An exhaustive conformer search using molecular mechanics yielded an initial set of geometries. These structures were further refined with high-level ab initio electronic structure calculations. Herein we report geometries and relative energies of 22 TMS conformers. The conformations are rationalized in terms of rotational potential energy surfaces in simple compounds, intramolecular C−H···O hydrogen bonding, and dipole−dipole repulsion.

Methodology

An exhaustive conformational search was performed at the molecular mechanics level using MM3(96)[8] with the default parameter set modified to reproduce the Csp^2−Csp^3 rotational potentials in aliphatic amides.[3] The search was done with the Saunders' stochastic search algorithm[9] that is present as a subroutine in MM3. This search yielded 22 minima after 5000 cycles. A second search, from a different starting geometry, yielded the same 22 minima. Structures from this search provided initial geometries for the electronic structure calculations.

SCHEME 1



N,N,N',N' - tetramethylsuccinamide (TMS)

Geometries of all conformers were optimized at the density functional theory (DFT) level with the DGauss program system.[10] These calculations were done with the DZVP2 basis set and the A2 fitting basis set.[11] The gradient-corrected approximation with the combination of the Becke exchange functional[12] and the Perdew correlation functional[13] was used. The structures were characterized by computing second derivatives. The absence of imaginary (negative) frequencies confirmed all structures to be minima. Single-point energy calculations at the optimum DFT geometries were done at the second-order Møller−Plesset (MP2) level[14] with the GAUSSIAN98 program system[15] and a polarized double-ζ basis set augmented by diffuse s and p functions on C, N, and O and diffuse s functions on H (MP2/DZP+diff).[16] Full geometry optimization at the MP2/DZP+diff level was done for the first four lowest energy conformers. Finally, single-point energies on the four MP2/DZP+diff geometries were done using the aug-cc-pVTZ basis set[17] and the computer program NWChem.[18] All MP2 calculations were done with the core electrons frozen.

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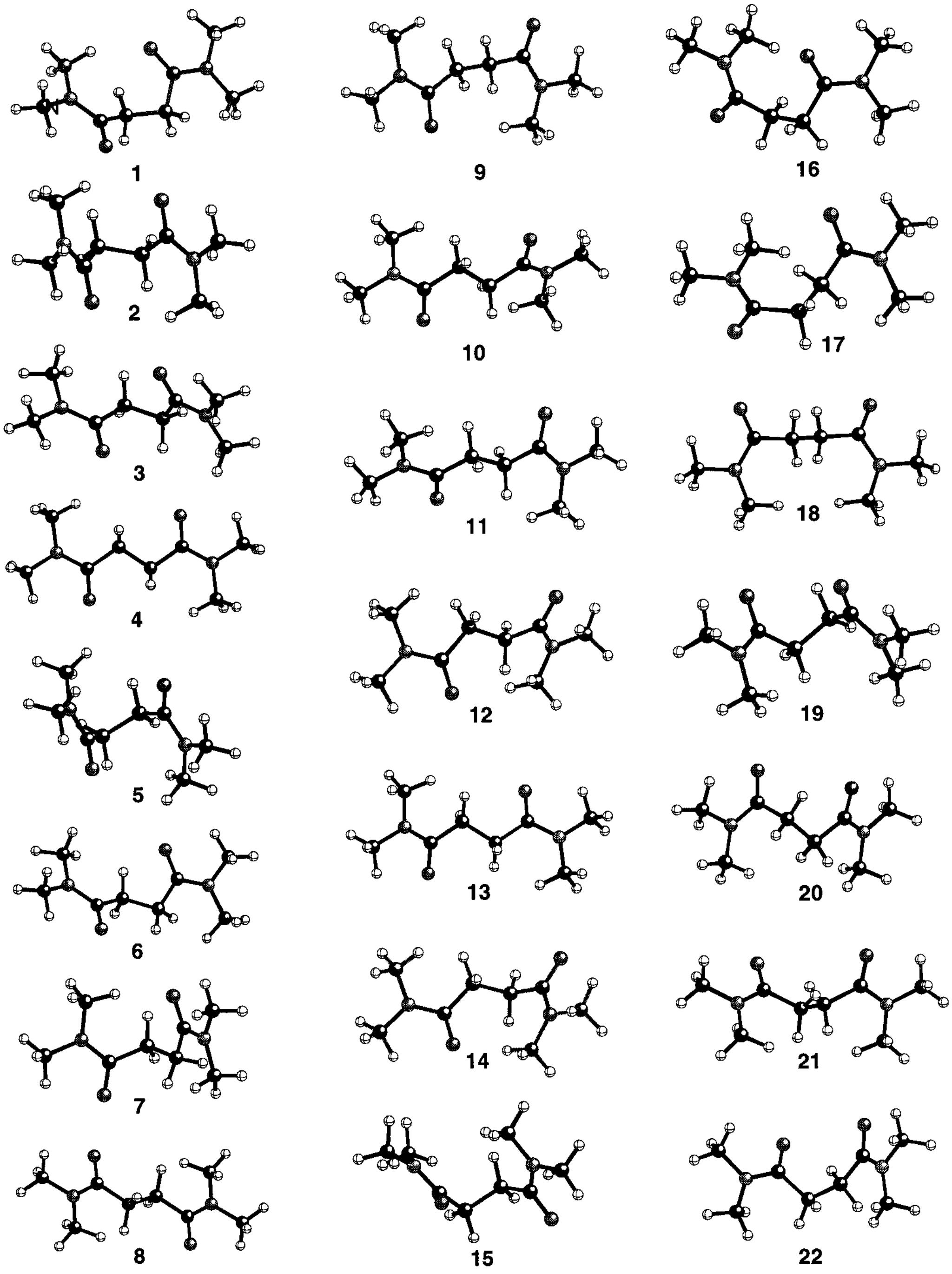


Figure 1. 22 conformers found at the MM3 and DFT levels of theory.

Results and Discussion

A total of 22 stable TMS geometries were located with MM3 calculations (Figure 1). In all cases, subsequent geometry optimization with DFT yielded stationary point structures that were close to the starting structures,[19] and analysis of the second derivatives confirmed these structures to be minima on the DFT potential surface. Given that the heavy atoms of each amide group, $(CH_3)_2N-C(=O)CH_2-$, are essentially coplanar, TMS conformers are distinguished by the degree of rotation about three C−C bonds, i.e., the dihedral angles for O8═C2−C3−C4, C2−C3−C4−C5, and C3−C4−C5═O7 (see Scheme 1 for atomic numbering scheme). Table 1 lists these dihedral angles at the DFT level, relative energies at all calculation levels, and dipole moments from the electronic structure calculations (Cartesian coordinates for the DFT optimized structures **1**−**22** are available as Supporting Information). Entries in Table 1 are rank-ordered with respect to the single-point MP2 energies obtained using the DFT geometries.

Conformations observed in larger molecules can often be understood in terms of the conformations observed in smaller molecules. We begin our discussion of the results with comparisons of the C−C dihedral angles in TMS with those in simpler systems. The dihedral angle distributions for each type of C−C bond are shown in Figure 2. The distribution of dihedral angles for C2−C3−C4−C5 (Figure 2a) reveals a significant population of both anti and gauche orientation of the amide substituents. This result is consistent with the expected behavior for rotation about Csp^3-Csp^3 bonds. On the basis of the behavior of normal alkanes, in which the anti configuration is ~0.9 kcal/mol more stable than the gauche configuration,[20] one would

TABLE 1: Dihedral Angles at the DFT Level, Relative Energies at All Levels of Theory, and Dipole Moments at the DFT and MP2 Levels[a]

conformer	O8−C2−C3−C4	C2−C3−C4−C5	C3−C4−C5−O7	ΔE (MM3)	ΔE (DFT)	ΔE (MP2)[b]	μ (DFT)	μ (MP2)
1	8.8	78.4	54.9	2.6	1.06	0.00 (0.00)	2.59	2.93
2	51.3	63.8	51.3	2.7	2.29	0.03 (0.02)	0.53	0.87
3	15.2	75.9	17.4	2.2	0.64	0.06 (0.41)	1.99	2.60
4	−2.5	179.4	−1.4	0.0	0.00	1.05 (1.86)	0.07	0.43
5	−103.3	27.3	−103.3	3.9	4.47	1.28	2.23	3.04
6	7.4	92.1	31.0	5.0	1.18	1.82	1.63	2.08
7	14.1	100.3	73.7	3.9	2.39	2.14	3.36	3.28
8	−89.3	180.0	89.3	1.6	2.71	2.21	0.00	0.00
9	−81.2	155.3	96.3	1.7	3.18	2.47	2.08	2.16
10	−6.1	178.0	87.0	1.3	2.23	2.71	4.89	4.98
11	−10.4	178.0	80.8	2.9	2.30	2.86	4.43	4.50
12	−14.8	131.9	97.1	1.4	2.91	2.94	4.71	4.68
13	46.0	179.2	−1.1	2.2	1.14	3.08	2.73	2.16
14	−101.2	51.6	−101.2	4.1	5.03	3.21	3.98	4.75
15	−94.7	77.2	82.9	3.4	5.81	3.48	6.13	6.45
16	66.4	79.0	−64.1	5.0	6.10	4.76	5.76	6.18
17	−103.1	113.0	90.4	3.8	6.33	5.09	4.52	4.71
18	−78.7	174.9	−78.7	3.5	5.40	5.32	7.44	7.67
19	47.7	75.4	−94.2	4.7	6.78	6.06	6.60	7.02
20	−106.1	85.6	21.7	4.6	6.96	6.48	6.98	7.43
21	−113.0	121.1	−112.4	5.5	7.49	7.40	6.29	6.79
22	−63.4	70.8	−114.9	6.7	8.66	7.98	6.00	6.71

[a] Angles in degrees, ΔE in kcal mol^{-1}, and μ in Debyes. [b] MP2 relative energies are from single point calculations at DFT geometries, quantities in parentheses are relative energies from full MP2 geometry optimizations. The lowest single point MP2 energy was −572.7985013 a.u. and the lowest optimized MP2 energy was −572.8015133 a.u.

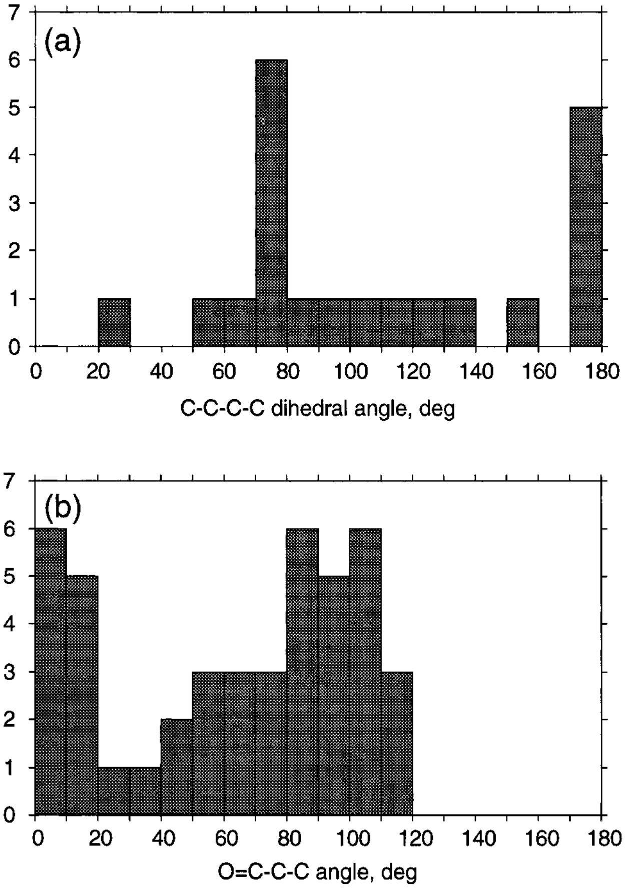


Figure 2. Distribution of absolute values for (a) C−C−C−C and (b) O═C−C−C dihedral angles calculated with DFT.

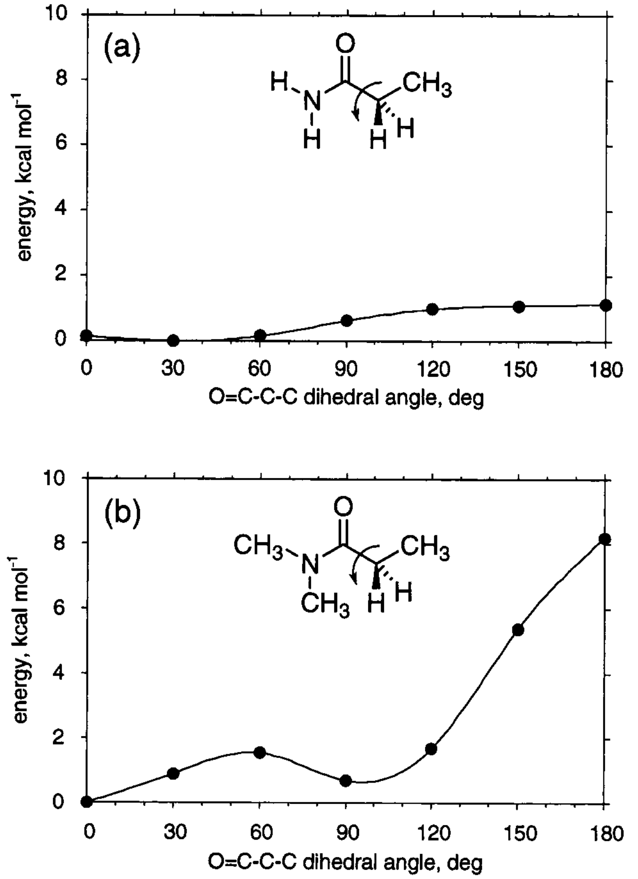


Figure 3. Potential energy surface for the O═C−C−C dihedral angle in (a) propanamide and (b) *N*,*N*-dimethylpronamide. The same scale has been used in both plots to emphasize the differences between the barriers in the two molecules.

predict that the lowest energy conformations of TMS should exhibit C2−C3−C4−C5 dihedral angles of 180°.

The distribution of dihedral angles for O8═C2−C3−C4 and C3−C4−C5═O7 (Figure 2b) indicates two preferred orientations, in the regions of 0° and 90°. This result is inconsistent with our prior studies on propanamide, $H_2NC(=O)CH_2CH_3$, where the rotational potential energy surface (PES) for rotation about the Csp^2−Csp^3 bond exhibits a single minimum located at 30°.[3] A likely reason for the discrepancy is the difference in nitrogen substitution, i.e., NH_2 in propanamide vs $N(CH_3)_2$ in

TABLE 2: Optimized DFT/DZVP2 and MP2/DZP+diff Geometries for 1−4[a]

	1		**2**		**3**		**4**		
parameter	DFT	MP2	DFT	MP2	DFT	MP2	DFT	MP2[b]	exp[20]
N1−C2	1.378	1.373	1.376	1.369	1.381	1.373	1.383	1.377 (1.367)	1.349
N1−C9	1.462	1.457	1.462	1.458	1.461	1.457	1.461	1.456 (1.458)	1.460
N1−C10	1.464	1.455	1.469	1.462	1.459	1.456	1.459	1.455 (1.457)	1.454
C2−C3	1.532	1.528	1.533	1.524	1.537	1.530	1.533	1.527 (1.533)	1.520
C2−O8	1.251	1.245	1.253	1.248	1.249	1.243	1.250	1.243 (1.233)	1.231
C3−C4	1.536	1.528	1.542	1.541	1.531	1.524	1.530	1.524 (1.530)	1.523
C4−C5	1.536	1.527	1.533	1.524	1.537	1.530	1.532	1.527 (1.533)	1.520
C5−N6	1.376	1.371	1.376	1.369	1.381	1.373	1.384	1.377 (1.383)	1.349
C5−O7	1.252	1.245	1.253	1.248	1.249	1.243	1.249	1.243 (1.233)	1.231
N6−C15	1.468	1.462	1.469	1.462	1.462	1.456	1.459	1.455 (1.457)	1.454
N6−C16	1.462	1.459	1.462	1.458	1.461	1.457	1.461	1.456 (1.468)	1.460
C2−N1−C9	119.0	119.1	118.8	118.8	118.8	118.9	119.1	119.1	120.1
C2−N1−C10	123.2	123.5	124.0	124.9	124.9	123.2	125.0	124.3	124.6
C9−N1−C10	117.4	115.8	117.2	116.2	116.0	116.0	115.8	115.4	114.8
N1−C2−C3	116.7	117.0	118.1	118.5	117.6	116.8	117.2	116.6	117.4
N1−C2−O8	121.9	122.1	122.2	122.4	121.6	116.8	121.5	121.9	121.7
C3−C2−O8	121.4	120.9	119.7	119.1	120.8	122.3	121.3	121.5	121.0
C2−C3−C4	111.8	109.8	110.1	108.9	110.6	120.8	111.2	110.8	111.5
C3−C4−C5	111.7	108.7	110.1	108.9	111.0	109.2	111.4	110.8	111.5
C4−C5−N6	118.5	118.3	118.1	118.5	116.8	116.9	116.9	116.6	117.4
C4−C5−O7	119.2	119.2	119.7	119.1	121.2	120.8	121.5	121.5	121.0
N6−C5−O7	122.2	122.4	122.2	122.4	122.0	122.3	121.6	121.9	121.7
C5−N6−C15	124.2	122.7	124.0	124.9	123.8	123.2	124.6	124.2	124.7
C5−N6−C16	118.6	117.7	118.8	118.8	119.1	118.8	119.0	119.1	120.1
C15−N6−C16	117.0	116.2	117.2	116.2	116.2	116.1	115.9	115.4	114.8
C9−N1−C2−C3	−176.7	−174.0	177.7	176.6	−175.2	−173.2	176.9	175.6	−176.9
C9−N1−C2−O8	4.1	7.2	−1.9	−5.3	6.0	8.8	−3.0	−5.4	3.5
C10−N1−C2−C3	−4.7	−9.2	−4.4	0.3	−1.8	−9.3	1.4	8.8	−5.1
C10−N1−C2−O8	176.1	172.0	175.9	178.4	179.4	172.7	−178.5	−172.2	175.3
N1−C2−C3−C4	172.0	174.3	129.0	111.8	166.0	165.8	177.6	179.5	−172.2
O8−C2−C3−C4	−8.8	−6.9	−51.3	−66.4	−15.2	−16.2	−2.5	0.4	7.3
C2−C3−C4−C5	−78.4	−65.8	−63.8	−61.1	−75.9	−66.8	179.4	179.5	180.0
C3−C4−C5−N6	128.2	138.1	129.0	111.8	164.3	162.9	178.6	179.4	172.2
C3−C4−C5−O7	−54.9	−44.5	−51.3	−66.4	−17.4	−19.2	−1.4	0.4	−7.3
C4−C5−N6−C15	−11.5	−16.1	−4.4	0.3	−5.6	−9.6	3.7	8.8	5.2
C4−C5−N6−C16	173.2	−174.5	177.7	176.6	−173.9	−173.1	175.3	175.6	172.9
O7−C5−N6−C15	171.7	166.5	175.9	178.4	176.2	172.6	−176.3	−172.2	−175.3
O7−C5−N6−C16	−3.6	8.1	−2.0	−5.3	7.8	9.0	−4.7	−5.4	−3.5

[a] Only parameters for heavy atoms are given. Distances in Å, angles in degrees. [b] The numbers in parentheses are distances that have been scaled to allow comparison to X-ray data.[22]

TMS. To examine the influence of nitrogen substitution, we calculated the PES for Csp^2−Csp^3 bond rotation in *N*,*N*-dimethylpropanamide, $(CH_3)_2NC({=}O)CH_2CH_3$, at the MP2/DZP level by freezing the O═C−C−C dihedral angle and optimizing the remaining geometric variables. As shown in Figure 3, replacement of NH$_2$ with N(CH$_3$)$_2$ dramatically changes the PES. In contrast to the relatively flat, low-energy PES found for propanamide, the *N*,*N*-dimethylpropanamide PES exhibits minima at both 0 and 90°, and after 120° the energy increases rapidly to a barrier height of 8 kcal/mol at 180°. This result is consistent with the distribution of dihedral angles shown in Figure 2b. On the basis of the behavior of *N*,*N*-dimethylpropanamide, one would predict that the lowest energy conformations of TMS should exhibit O8═C2−C3−C4 and C3−C4−C5═O7 dihedral angles of 0°.

Thus, on the basis of the conformational behavior in simple alkanes and *N*,*N*-dimethylpropanamide, we expect that the lowest energy conformation of TMS should have O8═C2−C3−C4, C2−C3−C4−C5, and C3−C4−C5═O7 dihedral angles of 0, 180, and 0°, respectively. Consistent with this simple model, both MM3 and gradient-corrected DFT find this conformation, **4** (Table 1), to be lowest in energy. In addition, this conformer is observed in the only crystal structure of TMS.[21] However, the single-point MP2 energies at the DFT geometries suggest that three conformers are energetically more stable than **4**! Moreover, examination of Table 1 reveals significant differences between the MP2 and DFT energies. For example, DFT gives an energy ordering of **4** < **3** < **1** < **13** < **6** < **10** < **2** < **11** < **7** < **8**. At the DFT level the two conformers **13** and **6** are very close in energy to **1**, being only 1.14 and 1.18 kcal/mol above **4**, respectively, and **2** is 2.29 kcal/mol higher than **4**.

To more firmly establish the relative energies of the most stable conformations, full MP2 geometry optimizations were performed on **1**−**4** (Cartesian coordinates for the MP2 optimized structures **1**−**4** are available as Supporting Information). Table 2 provides a comparison of structural parameters obtained at the MP2 level with the corresponding DFT values and, in the case of **4**, with experimental values. Taking absolute differences between the MP2 and DFT geometry parameters, we find a standard deviation in distances of 0.006 Å, bond angles of 1.1°, and dihedral angles of 3.9°, suggesting the overall differences between geometries at the two levels of theory to be small. However, we note that in some cases, e.g., **2**, further optimization at the MP2 level did yield changes in individual dihedral angles of up to 15°. After the MP2 distances were scaled using a previously reported method,[22] comparison between MP2 and experimental structural features reveals a good agreement with absolute standard deviations in distances of 0.009 Å, in bond angles of 0.25°, and in torsion angles of 3.85°.

Complete geometry optimization at the MP2/DZP+diff level does not change the relative ordering of the lowest energy conformers (see Table 1). Conformers **1** and **2** remain essentially

TABLE 3: Structural Parameters for C−H···O Interactions in 1−4[a]

	interaction	r (H···O)	r (C···O)	θ (C=O···H)	θ (C−H···O)
1	O7−C3	2.48	2.81	83.9	95.9
	O7−C16	2.28	2.73	84.3	102.3
	O8−C4	2.59	2.71	82.5	84.6
	O8−C9	2.27	2.76	84.5	104.6
	O8−C15	2.52	3.29	137.3	125.3
2	O7−C16, O8−C9	2.25	2.75	84.4	105.4
	O7−C10, O8−C15	2.38	3.34	100.8	146.6
3	O7−C3	2.47	2.72	85.1	91.4
	O7−C16	2.27	2.75	84.4	104.7
	O8−C4	2.48	2.72	84.8	90.5
	O8−C9	2.27	2.75	84.4	104.7
4	O7−C3a, O8−C4a	2.65	2.74	80.4	83.0
	O7−C3b, O8−C4b	2.66	2.74	80.0	82.6
	O7−C16, O8−C9	2.27	2.75	84.8	104.6

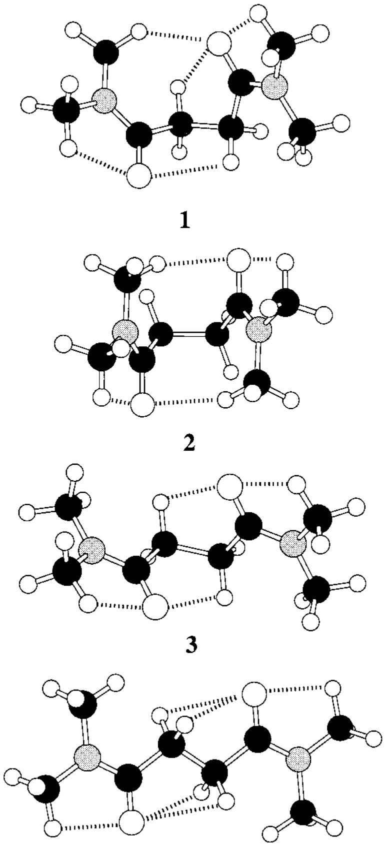
[a] Distances in Å, angles in degrees. In **4**, the a and b specify the two different hydrogen atoms on the methylene group.

isoenergetic, whereas conformer **3** is now 0.41 kcal/mol higher in energy. The largest change in relative energy is found for conformer **4**, which becomes 1.86 kcal/mol less stable than conformer **1**.[23] Going to a higher level of theory, single-point MP2/aug-cc-pVTZ calculations at the MP2/DZP+diff geometries, we found **2** to be the most stable conformer with **1** and **3** now 0.42 and 0.88 kcal/mol higher in energy, respectively. Thus, conformers **1**−**3** remain very similar in energy. However, **4** is now 2.37 kcal/mol higher in energy than **2**. These results clearly demonstrate that **4** is not the global minimum conformation for an isolated TMS molecule.

The MP2 calculations yield a different quantitative result as compared to the MM3 and gradient-corrected DFT calculations. Examination of the MP2/DZP+diff optimized geometries of **1**−**4** reveals that each of these structures contains multiple short C−H···O interactions that can be classified as C−H···O hydrogen bonds (see Figure 4). Structural parameters associated with these interactions are summarized in Table 3 for all contacts within 2.7 Å involving O, H pairs separated by three or more connected atoms. All four structures are similar in that they each exhibit C−H···O hydrogen bonds involving proximal N−CH_3 groups to form two five-membered ring structures. Each conformer also exhibits additional C−H···O interactions involving either β-methylene hydrogens or distal N−CH_3 groups.

The observed orientations can be compared with the ideal geometry for the C−H···O=C hydrogen bond on the basis of the results of crystal structure survey[4,24] and electronic structure calculations.[25] Experimental and theoretical evidence both suggest that the strongest hydrogen bond would be formed when the C−H···O angle is linear and the C=O···H angle is 120°. Although none of the C−H···O hydrogen bonds in **1**−**4** represent the ideal geometry, such interactions can still give rise to significant stabilization. Calculations on *N*,*N*-dimethylformamide dimers yield C=O···H(CH_2)−N interaction energies of −2.07 to −2.23 kcal/mol for orientations with C−H···O angles of 124−143° and C=O···H angles of 103−145°.[4] This result is consistent with the recent report of potential energy surfaces demonstrating that the weaker C−H···O hydrogen bonds are less sensitive to deviations from ideal geometry than the somewhat stronger HO···H hydrogen bonds.[25] On the basis of deviations from the ideal geometry, we make the qualitative observation that the C−H···O interactions found in **1** and **2** should be stronger than those found in **3** and **4**.

The additional stabilization provided by intramolecular C−H···O interactions provides an explanation for the relative energies obtained at the MP2 level of theory. In addition, significant contributions from C−H···O hydrogen bonding would account for the differences with the other levels of theory.


1

2

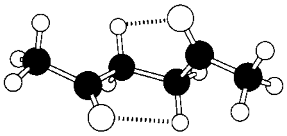
3

4

Figure 4. Optimized MP2 geometries for **1**, **2**, **3**, and **4**. Hashed lines indicate C−H···O interactions for all contacts within 2.7 Å involving O, H pairs separated by three or more connected atoms.

We have shown that gradient-corrected DFT methods, such as the one used in this study, can significantly underestimate the strength of C−H···O interactions.[4] Similarly, the MM3(96) model does not explicitly contain C−H···O hydrogen bonding, and, given the fact that all C−H bonds in TMS are assigned a zero bond moment, normal van der Waals interactions are the only nonbonded interactions to be included between O, H pairs. We note that the energy differences for conformers **1**−**4** are small, <2.5 kcal mol^{-1}. It is not surprising that the DFT results differ from the MP2 results given the small energy differences, as the MP2 method can reliably predict the energetics of hydrogen bonds[4,26] whereas the DFT methods do not predict hydrogen bond energies as well.[27]

Finally, we note that electrostatics also plays a role in determining the relative energies of TMS conformations. The



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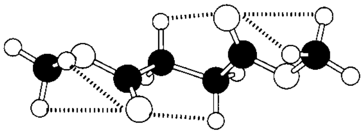

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Figure 5. HF geometries reported for 2,5-hexanedione, **23**,[28] and dimethylsuccinate, **24**.[29] Hashed lines indicate C−H···O interactions for all contacts within 2.7 Å involving O, H pairs separated by three or more connected atoms.

overall dipole moment can be used to qualitatively differentiate low-energy from high-energy conformers (see Table 1). The higher energy conformers have high dipole moments, whereas the lower energy conformers tend to have dipole moments less than 3 D and C═O groups in a trans configuration (see Figure 2).

It is of interest to compare our results on TMS with the results of conformational analyses reported for 2,5-hexanedione, **23**,[28] and dimethylsuccinate, **24**.[29] These two compounds present some important similarities with TMS in that (i) they contain two carbonyl groups separated by two methylene carbons, (ii) the all-trans form, analogous to **4**, is a local minimum, and (iii) at least one lower energy conformer exists in which the Csp^3-Csp^3 bond is gauche. In both **23** and **24**, the trans−gauche−trans conformation, analogous to **3**, was found to be the most stable one. MP2/6-31G(d) single-point energies on HF/6-31G(d) optimized geometries yielded an energy difference between the trans−gauche−trans form and the all-trans form of 1.7 and 1.6 kcal/mol, respectively.[26,27] These differences are similar to the difference, 1.9 kcal/mol, calculated here for the analogous TMS conformations, **3** and **4**. Examination of the trans−gauche−trans forms of **23** and **24** (see Figure 5) reveals the presence of close contacts between the methylene hydrogen atoms and the carbonyl oxygen atoms, 2.60 Å in **23** and 2.61 Å in **24**, suggesting that, as with **3**, C−H···O interactions also play an important role in stabilizing these structures. We note that the HF/6-31G(d) C−H···O distances in **23** and **24** are longer than the 2.47 Å distance obtained for **3** at the MP2/dzp+diff level. In prior calculations, we have observed a similar shortening of C−H···O distances on going from the HF level to the MP2 level.[4]

Conclusions

This study has identified 22 gas-phase minima for TMS. The most stable gas-phase conformer does not correspond to the one observed experimentally in the solid state. In the gas phase, normally unfavorable rotations about the C−C bonds allow C−H···O hydrogen bonds to form, which give extra stabilization to some conformers. The all-trans conformer **4**, which most resembles the structure observed by X-ray diffraction, is 2.37 kcal/mol less stable than the lowest energy conformer.

Comparison of the structures and energies of the results at the two ab initio levels shows that the geometries predicted at the gradient-corrected DFT level are very similar to those found at the MP2 level. However, the relative energies of the conformers are different, probably owing to the known inability of DFT to properly account for the hydrogen bond energies in the different conformers. It is likely that the MM3 relative energies could be improved if C−H···O hydrogen bond interactions were included in the force field. We are working on reparametrizing the MM3 force field to properly account for such nonbonded interactions.

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Supporting Information Available: Cartesian coordinates for the DFT optimized structures **1**−**22** and MP2 optimized structures **1**−**4** (ASCII). This material is available free of charge via the Internet at http://pubs.acs.org.

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