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Molecular mechanics (MM3) study of organogermanes

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ABSTRACT: The MM3 force field has been extended to permit the treatment of organogermanes. The vibrational spectra, molecular structures, moments of inertia, dipole moments and conformational energies of 21 compounds were studied. The available experimental data are mostly well reproduced. Copyright © 1999 John Wiley & Sons, Ltd.

KEYWORDS: molecular mechanics; MM3 force field; organogermanes

INTRODUCTION

Molecular mechanics has become a powerful tool for studying molecular structures and conformational energies during the past two decades. The MM2 force field, which has been widely used, gives generally good results for structures and energies for a wide variety of compounds.[1] A previous MM2 study on Group IV organometallanes (germanium, tin, and lead) has been published.[2] However, early versions of MM2 gave some minor errors, which were later corrected. Nevertheless, there still appear to be some significant systematic errors, and it would require substantial efforts to fix them. Instead of trying to revise the MM2 force field, a new force field (called MM3)[1] was instead developed.[3] The MM3 force field has been applied to a variety of compounds including hydrocarbons,[3] alkenes,[4] alcohols and ethers,[5] aldehydes and ketones,[6] amines,[7] conjugated alkenes,[8] nitro compounds,[9] sulfides,[10] disulfides[11] and conjugated carbonyls.[12] In this paper, we are concerned with the extension of MM3 force field to deal with the organogermanes.

Unlike MM2, which fit structures and energies only, we would also like to reproduce the vibrational spectra here and these were studied first, using approximate structures as obtained from MM2 parameters. This fairly well determined the force parameters. We then adjusted the other parameters, such as natural bond lengths, bond angles, bond moments, etc., to give the best fit to the experimental structures, conformational energies and rotational barriers. Organogermanes, which are the analogs of the silanes and corresponding hydrocarbons, usually are tetrahedral with threefold rotational barriers. In silanes, the bond lengths showed significant electronegativity effects, whereas in germanes the electronegativity effect is still present, but it is much less significant. The vibrational spectra of six compounds, and the molecular structures, dipole moments and rotational barriers of 11 compounds were examined. The final parameter set derived is listed in Table 1.

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RESULTS AND DISCUSSION

Vibrational spectra

There are eight organogermanes that have been studied spectroscopically.[13–22] Those are germane, methylgermane, trimethylgermane, ethylgermane, vinylgermane, cyclobutylgermane, germacyclopentane and phenylgermane. From previous experience,[3–12] in order to fit the spectra better, some cross-terms such as the torsion–bend–bend interaction are needed. However, such terms are not part of the MM3 force field. We therefore accept the resulting errors. The MM3-calculated vibrational spectra for these eight germanes are summarized in the Tables 2–9. The average MM3 Ge–H and Ge–C stretching modes are 2085 cm^{-1} (over 18 bonds) and 547 cm^{-1} (over eight bonds), compared with the experimental values of 2084 and 551 cm^{-1}, respectively. The skeletal bending modes, GeCC and CGeC, which are experimentally in the region averaging around 239 cm^{-1}, are also well reproduced by MM3, 244 cm^{-1}. However, the modes involving hydrogen bendings show problems similar to those previously found with other compounds. Normally, the asymmetric and symmetric GeH_3 deformations are in the region of 900 and 800 cm^{-1}, respectively. There is a troublesome mode in vinylgermane, the CH_2 rock, which was experimentally assigned

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Table 1. The MM3 parameter set for organogermanes[a,b]

Stretching parameters		
Bond	k_s	l_0
1–31	2.72	1.949
5–31	2.55	1.529
2–31	3.58	1.935
22–31	2.70	1.911
31–31	1.45	2.404
1–31[c]	2.95	1.944
31–56	2.05	1.944

Bending parameters			
Angle	k_θ	θ_0	Type
5–31–5	0.423	107.5	1
		108.5	2
		109.5	3
1–31–5	0.390	110.2	1
		110.5	2
		111.5	3
5–1–31	0.420	110.0	1
		111.9	2
		110.0	3
1–31–1	0.500	109.5	1
		109.8	2
		110.5	3
1–1–31	0.450	109.3	
2–2–31	0.250	119.1	
5–2–31	0.510	120.0	
2–31–5	0.390	110.1	
2–31–2	0.500	109.5	
22–22–31	0.500	117.0	
5–22–31	0.400	119.0	
5–31–22	0.400	108.8	
5–31–31	0.350	114.5	
2–31–31	0.500	109.5	
1–1–31[c]	0.680	105.5	
1–31–1[c]	0.570	100.0	
5–31–56	0.510	105.2	
5–56–31	0.400	110.2	
31–56–56	0.460	110.0	
2–31	0.10		

Torsional parameters			
Dihedral angle	V_1	V_2	V_3
5–1–31–1	0.000	0.000	0.127
5–1–31–5	0.000	0.000	0.132
1–1–31–5	0.000	0.000	0.172
5–1–1–31	0.000	0.000	0.185
1–1–31–1	−0.200	0.085	0.112
1–1–1–31	−0.200	0.000	0.112
2–2–31–5	0.000	0.000	−0.245
5–2–31–5	0.000	0.000	0.175
5–2–2–31	0.000	6.450	0.000
2–2–2–31	0.000	6.450	0.000
22–22–22–31	0.000	0.000	0.132
22–22–31–5	0.000	0.000	0.285
5–22–31–5	0.000	0.000	0.285
5–22–22–31	0.000	0.000	0.132
5–31–31–5	0.000	0.000	0.165
2–2–31–31	0.000	0.000	0.132
2–31–31–2	0.000	0.000	0.132
1–1–1–31[b]	−0.200	0.000	0.520

Table 1. (continued)

Torsional parameters			
Dihedral angle	V_1	V_2	V_3
2–2–31–2	0.000	0.000	0.132
5–2–31–2	0.000	0.000	0.175
5–31–56–5	0.000	0.000	0.130
5–31–56–56	0.000	0.000	0.130
5–56–56–31	0.000	0.000	0.110
31–56–56–56	0.000	0.000	0.110
1–1–1–31[c]	0.000	0.000	0.520

Bond moment parameters	
Bond	Moment
1–31	−0.635
2–31	−1.120
22–31	−0.500
31–31	0.000
1–31[c]	−0.495

Van der Waals parameters		
Atom type	ϵ	r^*
31	0.200	2.440

Electronegativity correction			
Bond	End of bond	Atom type	Correction
5–31	31	31	0.006
2–2	2	31	0.002
5–31	31	1	0.008

Stretch–bend parameter	
Atom type	k_{sb}
X—Ge—Y	0.45
X—Ge—H	0.00

[a] The atom type numbers are those used in MM3; 1 is saturated carbon, 2 is unsaturated carbon, 5 is hydrogen, 22 is three-membered ring carbon, 31 is germanium and 56 is four-membered ring carbon. X and Y are heavy atoms.
[b] Some values in this parameter set are somewhat different from those in MM3(96). The values marked with an asterisk in MM3(96) were only preliminary and if that version of MM3 is used for calculations on organogermanes, the parameters given in the tables should be read in. These parameters will be included in MM3(99) and later versions.
[c] Parameter for five-membered ring.

at 877 cm^{-1}, while MM3 gives 1050 cm^{-1}. However, there was another mode, the GeH_3 deformation, was also assigned at 887 cm^{-1} which turned out to be reasonable for germyl deformation. We believe that there might be a frequency missed or simply misassigned. The calculated spectrum of germacyclopentane has several vibrations with very large errors, especially an '*A*' symmetry ring C–C stretching mode which is 177 cm^{-1} too high and a '*B*' symmetry CH_2 rock mode which is 219 cm^{-1} too low. The r.m.s. error is calculated to be 56 cm^{-1}, which is much larger than we would like to have, and the average

Table 2. Vibrational spectra of germane

Symmetry	No.	Exptl[13]	MM3	Δ	Assignment
A_1	1	2111	2071	−40	Sym. Ge–H str.
E	2	931	956	25	GeH_3 def.
T_2	3	2111	2090	−21	Asym. Ge–H str.
	4	821	795	−26	GeH_3 def.
R.m.s.				26	
Av.				−15	

Table 3. Vibrational spectra of methylgermane

Symmetry	No.	Exptl[15]	MM3	Δ	Assignment
A_1	1	2938	2882	−56	Sym. C–H str.
	2	2085	2076	−9	Sym. Ge–H str.
	3	1254	1225	−29	CH_3 def.
	4	843	770	−73	GeH_3 def.
	5	602	601	−1	Ge–C str.
A_2	6	155	175	20	Ge–C torsion
E	7	2997	2981	−16	C–H str.
	8	2084	2089	5	Ge–H str.
	9	1428	1418	−10	CH_3 def.
	10	900	907	7	GeH_3 def.
	11	848	799	−49	CH_3 rock
	12	506	544	36	GeH_3 rock
R.m.s.				31	
Av.				−11	

Table 4. Vibrational spectra of trimethylgermane

Symmetry	No.	Exptl[18]	MM3	Δ	Assignment
A_1	1	2982	2982	0	Asym. C–H str.
	2	2922	2882	−40	Asym. C–H str.
	3	2040	2084	44	Sym. Ge–H str.
	4	1426	1419	−7	Asym. CH_3 def.
	5	1246	1223	−23	Sym. CH_3 def.
	6	833	804	−29	Sym. CH_3 rock
	7	571[a]	559	−12	Sym. Ge–C str.
	8	187	171	−16	Sym. GeC_3 def.
A_2	9	—	2981	—	Asym. C–H str.
	10	—	1418	—	Asym. CH_3 def.
	11	—	793	—	CH_3 wag
	12	—	141	—	Ge–C torsion
E	13	2982	2982	0	Asym. C–H str.
	14		2981	−1	Asym. C–H str.
	15	2922	2882	−40	Asym. C–H str.
	16	1426	1418	−8	Asym. CH_3 def.
	17		1418	−8	Asym. CH_3 def.
	18	1246	1223	−23	Asym. CH_3 def.
	19	850[b]	803	—	Asym. CH_3 rock
	20	833	800	−33	Asym. CH_3 wag
	21	624[b]	712	—	CGeH bending
	22	592	599	19	Asym. Ge–C str.
	23	187	196	9	CGeC bending
	24	—	145	—	Ge–C torsion
R.m.s				20	
Av.				−9	

[a] Values taken from solid-state spectrum.
[b] Values taken from solid-state spectrum; two modes (850 and 624 cm^{-1}) were heavily coupled and reversely assigned. The MM3 assignments are given in the table.

Table 5. Vibrational spectra of ethylgermane

Symmetry	No.	Exptl[16]	MM3	Δ	Assignment
A'	1	2967	2964	−3	Asym. CH_3 str.
	2	2931	2882	−49	Sym. CH_3, CH_2 str.
	3	2885	2868	−17	Asym. CH_3, CH_2 str.
	4	2079	2090	11	Asym. Ge–H str.
	5		2076	−3	Sym. Ge–H str.
	6	1470	1456	−14	Asym. CH_3 def.
	7	1422	1441	19	Asym. CH_3 def., CH_2 sci.
	8	1379	1404	25	Asym. CH_2 sci., CH_3 def.
	9	1232	1295	63	CH_2 rock
	10	1030	1002	−28	CH_3 rock
	11	974	967	−7	C–C str.
	12	888	903	15	GeH_3 def.
	13	836	769	−67	GeH_3 def.
	14	618	574	−44	Ge–C str., GeH_3 rock
	15	524	529	5	GeH_3 rock, Ge–C str.
	16	230	254	24	GeCC bending
A''	17	2970	2965	−5	Asym. CH_3 str.
	18	2957	2927	−32	Asym. CH_3 str.
	19	2085	2089	4	Asym. Ge–H str.
	20	1464	1467	3	Asym. CH_3 def.
	21	1238	1158	−80	CH_2 twist
	22	979	998	9	CH_3 wag
	23	880	906	26	GeH_3 def.
	24	723	750	27	CH_2 wag
	25	492	540	48	GeH_3 wag
	26	—	223	—	C–C torsion
	27	—	124	—	Ge–C torsion
R.m.s.				33	
Av.				−3	

error is −5 cm^{-1}. Next is cyclobutylgermane. At time the force field for cyclobutane was developed, the molecular structure and heat of formation were carefully reproduced, but the vibrational spectrum was not examined. Therefore, the force parameters for open-chain compounds were used, and those ring deformations (including stretching and bending) were not adequate. The r.m.s. and average errors for cyclobutane itself were later found to be 88 and −45 cm^{-1}. The MM3-calculated spectrum of cyclobutylgermane shows related large errors in the modes involving CH_2 bending (Table 7), although the r.m.s. and average errors are not so bad. The spectrum of phenylgermane was reported by During *et al.*[21] The symmetry assignment of this molecule by MM3 and by experiment are different. MM3 gives C_1 symmetry and experimental assignments were based on C_{2v} symmetry. In Table 9, we list the spectrum based on the MM3 vibrational motions, and ignore the symmetry. This spectrum was not included in statistical calculations. The r.m.s. and average errors of 176 vibrational frequencies over a set of seven germanes are 42 and −12 cm^{-1}, respectively. The small value of the latter indicates a lack of any serious systematic error, while the r.m.s. error is similar to that for hydrocarbons (35 cm^{-1}) and is about as

Table 6. Vibrational spectra of vinylgermane

Symmetry	No.	Exptl[19]	MM3	Δ	Assignment
A′	1	3066	3103	37	=CH_2 str.
	2	3003	3045	42	=CH str.
	3	2959	3007	48	=CH_2 str.
	4	2090	2089	−1	GeH_3 str.
	5		2076	−14	GeH_3 str.
	6	1595[a]	1602	7	C=C str.
	7	1398	1430	32	=CH_2 sci.
	8	1268	1225	−43	=CH in-plane-bending
	9	887[b]	1046	—	=CH_2 rock
	10	887	903	16	GeH_3 def.
	11	834	755	−79	GeH_3 def.
	12	639	639	0	Ge–C str.
	13	543	538	−5	GeH_3 wag
	14	267[a]	289	22	GeC=C bending
A″	15	2090	2090	0	GeH_3 str.
	16	1007	1062	55	=C–H out-of-plane bending
	17	950	906	−44	=CH_2 wag (out-of-plane bending)
	18	876	903	27	GeH_3 def.
	19	524	558	34	GeH_3 wag
	20	420	446	26	=CH_2 twist, GeH_3 twist
	21	—	127	—	Ge–C torsion
R.m.s.				35	
Av.				8	

[a] Values taken from liquid Raman spectrum.
[b] See text.

good as can be expected from a force field containing as few cross-terms as MM3.

Since germanium is slightly elecropositive, we might expect that its substitution into a hydrocarbon would cause the C—H bond lengths in methylgermane, for example, to stretch slightly. This stretching would be small and hard to measure directly, but the stretching frequencies of the C—H bonds can be used as a sensitive measure of bond length.[23] These show that C–H stretching is negligible. For ethylgermane, the stretching appears to be 0.011 Å, but the experimental error is 0.010 Å, and the stretching, if any, is too small to measure with certainty.

Structures and energies

MM3 is designed to reproduce gas-phase electron diffraction structures, which usually are given in r_g units.[3] Since the different experimental methods give structures in different units (r_g, r_α, r_s, etc.), it is important to compare the MM3 and experimental values in the same units. These various interconversions may be carried out using the MM3 program.[24] Therefore, throughout the present study, we converted the standard r_g values to the units reported in the individual experiments before making comparisons. There are several isotopes of germanium (^{70}Ge–^{76}Ge), a few of which have large and roughly equal natural abundances. Here we specifically used the moments of inertia corresponding to the principal isotope (^{74}Ge) to compare the calculated and experimental values. The molecular structures of orga-

Table 7. Vibrational spectrum of cyclobutylgermane (equatorial)

Symmetry	No.	Exptl[22]	MM3	Δ	Assignment
A′	1	2980	2983	2	γ-CH_2 str.
		3019[a]	2983	−36	
	2	2968	2978	10	β-CH_2 str.
		2961[a]	2978	17	
	3	2927	2920	−7	γ-CH_2 str.
		2935[a]	2931	−4	
	4	2919	2914	−5	α-CH str.
	5	2873	2899	26	β-CH_2 str.
		2879[a]	2900	21	
	6	2072	2089	17	GeH_3 str.
	7	2068	2075	7	GeH_3 str.
	8	1473	1383	−90	γ-CH_2 def.
	9	1451	1330	−121	β-CH_2 def.
	10	1262	1294	32	α-CH in-plane bend
		1269[a]	1262	−7	
	11	1231	1157	−74	β-CH_2 wag
		1236[a]	1169	−67	
	12	1201	1079	−22	β-CH_2 twist
	13	1067	1031	−36	Ring def.
		1036[a]	1021	−15	
	14	999	981	−17	Ring breathing
	15	883	895	12	GeH_3 def.
	16	853	878	25	β-CH_2 rock
	17	828	846	18	GeH_3 def.
	18	692	707	15	Ring def.
		708[a]	709	1	
	19	598	588	−10	γ-CH_2 rock
	20	588	562	−26	GeH_3 rock
		675[a,b]	496	—	
	21	440	410	−30	Ring-Ge str.
		484[a]	459	−25	
	22	262	261	−1	Ring-Ge bend
		260[a]	260	0	
	23	135	148	13	Ring puckering
		107[a]	130	23	
B	24	2956	2978	22	β-CH_2 str.
	25	2933	2908	−25	β-CH_2 str.
	26	2074	2090	16	GeH_3
	27	1443	1343	−100	β-CH_2 def.
	28	1251	1160	−91	γ-CH_2 wag
	29	1220	1123	−97	β-CH_2 wag
	30	1183	1050	−133	γ-CH_2 twist
	31	1081	1004	−77	β-CH_2 twist
	32	940	969	29	Ring def.
	33	924	929	5	α-CH bend
	34	876	864	−12	GeH_3 def.
	35	820	871	51	Ring def.
	36	779	851	72	β-CH_2 rock
	37	566	569	3	GeH_3 rock
	38	186	196	10	Ring-GeH_3 bend
	39	130	107	−23	GeH_3 torsion
R.m.s.				46	
Av.				−14	

[a] For axial conformer.
[b] This frequency was also assigned as a ring deformation.

Table 8. Vibrational spectra of germacyclopentane (C_2 twist)

Symmetry	No.	Exptl[20]	MM3	Δ	Assignment
A	1	2932[a]	2945	13	α-CH_2 str.
	2	2904[a]	2925	21	β-CH_2 str.
	3	2881	2891	10	α,β-CH_2 str.
	4	2865	2875	10	β,α-CH_2 str.
	5	2066	2081	15	Asym. GeH_2 str.
	6	1453	1453	0	Sym. β-CH_2 scissoring
	7	1419	1426	7	α-CH_2 scissoring
	8	1324	1377	53	β-CH_2 wag
	9	1246	1209	−27	α-CH_2 wag
	10	1200	1170	−30	β-CH_2 twist
	11	1078	1099	21	α-CH_2 twist
	12	848[a]	1025	177	C-C str.
	13	1025	941	−84	β-CH_2 rock
	14	881	837	−44	GeH_2 scissoring
	15	762	797	35	C-C str., GeH_2 scissoring
	16	785[b]	756	—	α-CH_2 rock
	17	635	623	−12	Ge-C str.
	18	543	596	53	GeH_2 twist
	19	345	296	−49	GeCC bending
	20	273[a]	284	11	CGeC bending
B	21	2978	2945	−33	α-CH_2 str.
	22	2946	2926	−20	β-CH_2 str.
	23	2936	2890	−46	α-CH_2 str.
	24	2922	2865	−57	β-CH_2 str.
	25	2066	2090	24	GeH_2 str.
	26	1455	1447	−8	Asym. β-CH_2 scissoring
	27	1429	1395	−34	α-CH_2 scissoring
	28	1312	1344	32	β-CH_2 wag
	29	1251	1205	−46	α-CH_2 wag
	30	1150	1191	41	β-CH_2 twist
	31	1033	1072	39	α-CH_2 twist
	32	946	947	1	C–C str.
	33	1057	838	−219	β-CH_2 rock
	34	804	776	−28	α-CH_2 rock
	35	694[a]	641	−53	GeH_2 wag
	36	589	567	−22	Ge–C str.
	37	481	474	−7	Ge–C str., GeH_2 rock
	38	431	469	38	GeH_2 rock
	39	113	110	−3	Ring puckering
R.m.s.				56	
Av.				−5	

[a] Values taken from liquid Raman spectrum.
[b] Estimated value, see Ref. 20.

Table 9. Vibrational spectra of phenylgermane

No.	Exptl[21]	MM3	Assignment
1	3082	3055	Ph–H str.
2	3069	3050	
3	3047	3045	
4	3022	3041	
5	3000	3038	
6	—	2090	Ge–H str.
7	2072	2089	
8		2076	
9	1583	1656	C=C str.
10	1571	1650	C=C str.
11	1482	1607	C=C str.
12	1433	1500	C=C str., Ph–H in-plane bending
13	1329	1429	Ph–H in-plane bending
14	1301	1326	Ph–H in-plane bending
15	1187	1222	Ph–H in-plane bending
16	1151	1202	Ph–H in-plane bending
17	968	1090	Ph–H out-of-plane bending
18	1096	1082	Ph–Ge str.
19	1026	1029	Ph–H in-plane bending
20	968[a]	1006	Ph–H out-of-plane bending
21	999	969	Ring def.
22	948[a]	921	Ring def., Ph–H out-of-plane bending
23	878	902	Asym. GeH_3 def.
24	—	897	Asym. GeH_3 def.
25	910	876	Ph–H out-of-plane bending
26	826	753	Sym. GeH_3 def.
27	738	734	Ph–H out-of-plane bending
28	673	668	In-plane ring def.
29	699	644	Ph–H out-of-plane bending, ring out-of-plane bending
30	619	601	In-plane Ring def.
31	—	586	Ph–H out-of-plane bending, ring out-of-plane bending
32	585	531	GeH_3 rock
33	580	530	GeH_3 wag
34	418	388	Ring out-of-plane bending
35	395	358	Ring out-of-plane bending
36	292	302	Ring def.
37	230	185	Ring-Ge in-plane bending
38	161	138	Ring-Ge out-of-plane bending
39	—	0	Ring-GeH_3 free rotation

[a] Estimated values.

nogermanes calculated by MM3 are listed in Tables 10–24, along with the observed data.

Germane. The rotational constant (B_0) of germane was determined based on the infrared spectrum.[25] The best value for B_0 was determined as 2.69587(7) cm^{-1}. The Ge—H bond length is accordingly computed to be 1.525358(20) Å (r_0). MM3 gives an r_z bond length, which should be close to r_0, of 1.522 Å.

Methylgermane. The structural parameters for methylgermane were determined by microwave spectroscopy.[26] The Ge—C and Ge—H bonds were 1.9453(5) and 1.529(5) Å (r_s), compared with 1.943 and 1.517 Å by MM3, respectively. The C—H bonds were determined as 1.083(5) Å and the MM3 value is 1.095 Å. Similarly to its silicon analog, methylsilane, the most stable conformer is the staggered form. The barrier to internal methyl rotation is 1.23 kcal mol^{-1} by MM3, and 1.24 kcal mol^{-1} by the microwave method (1 kcal = 4.184 kJ). The dipole moment of methylgermane was measured as 0.635(6) D from the Stark effect. The MM3-calculated dipole moment is 0.64 D. In Table 11, we summarize the experimental and MM3-calculated structures of methylgermane. The barriers to internal rotation and dipole moments of the organogermanes are listed in Tables 25 and 26, respectively.

Table 10. Molecular structure (r_0) of germane[a]

	Exptl[25]	MM3/Δ
Ge—H	1.5253	1.522/−0.003
HGeH	—	109.5/–
Moments of inertia[b]	Exptl[25]	MM3/%
$I_x = I_y = I_z$	6.253	6.2739/0.33

[a] Here and in subsequent tables, bond lengths in Å, angles in degrees.
[b] Atomic unit.

Table 11. Molecular structure (r_S) of methylgermane

	Exptl[26]	MM3/Δ
Ge—C	1.945(5)	1.943/−0.002
Ge—H	1.529(5)	1.517/−0.012
C—H	1.083(5)	1.095/0.012
HGeH (θ_S)	108.2(5)	108.0/−0.2
HCH	108.4(5)	108.2/−0.2
Moments of inertia[a]	Exptl[26]	MM3/%
I_x	9.376	9.3133/−0.67
$I_y = I_z$	58.445	58.6285/0.31

[a] Converted from rotational constants, $A'' = 1.798(25)\ cm^{-1}$, cited in Ref. 14.

Table 12. Molecular structure (r_0) of dimethylgermane

	Exptl[27]	MM3/Δ
Ge—C	1.950(3)	1.949/−0.001
C—H	1.083 (assumed)	1.101/–
HCH	108.5 (assumed)	108.2/–
CGeC	110.0(5)	109.9/−0.1
Moments of inertia	Exptl[27]	MM3/%
I_x[a]	40.3844	40.6281/0.60
I_y	90.4722	90.6939/0.25
I_z	118.5421	118.7043/0.14

[a] Rotational constants: $A = 12522.67$ MHz, $B = 5587.68$ MHz and $C = 4264.57$ MHz.

Table 13. Molecular structure (r_S) of trimethylgermane

	Exptl[28]	MM3/Δ
Ge—C	1.947(6)	1.946/−0.001
Ge—H	1.532(1)	1.525/−0.007
C—H	1.095 (assumed)	1.095/–
CGeC (θ_0)	109.6(1)	109.2/−0.4
GeCH	110.97 (assumed)	110.7/–
CGeH	109.3 (assumed)	109.7/–
Moments of inertia[a]	Exptl[28]	MM3/%
$I_x = I_y$	105.60	106.0489/0.43

[a] $B = 4785.88$ MHz.

Table 14. Molecular structure (r_g) of tetramethylgermane

	Exptl[29]	MM3/Δ
Ge—C	1.945(3)	1.949/0.004
C—H	1.12(2)	1.112/−0.008
GeCH	108(2)	110.7/2.7
CGeC	109.5 (fixed)	109.5/–
HCH	110.6(15)[a]	108.2/−2.4

[a] Dependent parameter.

Table 15. Molecular structure (r_0) of ethylgermane

	Exptl[16]	MM3/Δ
Ge—C	1.949(10)	1.957/0.008
Ge—H	1.522(10)	1.531/0.009
C_2—C_3	1.545(10)	1.534/−0.011
C_2—H	1.093(10)	1.103/0.010
C_3—H	1.091(10)	1.104/0.013
GeCC	112.16(75)	112.15/0.01
HGeH	108.59(75)	108.01/−0.58
GeC_2H	111.64(75)	110.05/−0.59
HGeC	109.74(75)	110.90/1.16
HC_2H	106.43(75)	106.47/0.04
HC_3H	108.04(75)	107.14/−0.90
C_3C_2H	107.87(75)	108.98/1.12
C_2C_3H	110.86(75)	111.71/1.05
Moments of inertia[a]	Exptl[16]	MM3/%
I_x	22.7099	22.7318/0.10
I_y	141.057	141.6021/0.39
I_z	151.350	151.8699/0.34

[a] Rotational constants: $A = 22254.227(378)$ MHz, $B = 3528.885(17)$ MHz, $C = 3339.232(16)$ MHz.

Table 16. Torsional energies of methylethyl- and propylgermane

		ΔE (kcal mol^{-1})		
Compound		Ouellette[34]	MM2	MM3
Methyethyl-	*cis*	0.96	1.25	1.31
	gauche	−0.21	−0.13	−0.09
	skew	1.26	1.30	1.33
	anti	0.00	0.00	0.00
Propyl-	*cis*	5.90	4.93	5.08
	gauche	0.46	0.62	0.64
	skew	3.49	2.58	2.78
	trans	0.00	0.00	0.00

Table 17. Conformational energies of *n*-methylgermacyclohexane

	ΔG[a] (kcal mol^{-1})		
Compound	MM2[b]	MM3	Exptl[33]
1-Methyl-	−0.25	−0.20	−0.24
2-Methyl-	0.89	1.10	—
3-Methyl-	1.34	1.94	—
4-Methyl-	1.41	1.97	—

[a] $\Delta G = G_{ax} - G_{eq}$.
[b] MM2 value is the difference in steric energies.

Table 18. Molecular structure (r_0) of vinylgermane

	Exptl[35]	MM3/Δ
Ge—C_2	1.926(12)	1.939/0.013
Ge—H	1.520(5)	1.520/0.000
C_2=C_3	1.347(15)	1.339/−0.008
C_2—H	1.094 (assumed)	1.092/–
C_3—H	1.097 (assumed)	1.090/–
GeCC	122.9(6)	122.67/−0.23
CGeH	109.7(6)	110.36/0.66
$C_2C_3H_4$	120.35 (assumed)	120.55/–
$C_2C_3H_5$	120.65 (assumed)	121.67/–
C_3C_2H	118.00 (assumed)	119.14/–
Moments of inertia[a]	Exptl[35]	MM3/%
I_x	15.4446	15.3543/−0.58
I_y	131.620	132.2862/0.51
I_z	140.896	141.5505/0.46

[a] Rotational constants: A = 32721.94 MHz, B = 3839.67 MHz, C = 3586.89 MHz.

Table 19. Molecular structure (r_a) of cyclopropylgermane

	Exptl[36]	MO[a,e,37]	MM3/Δ
Ge—C_1	1.924(2)	1.9227	1.925/0.001
Ge—H av.	1.530[b]	1.546	1.524/−0.006
C_1—C_2	1.521(7)	1.5253	1.514/−0.007
C_2—C_3	1.502(9)	1.5086	1.510/0.008
C—H av.	1.091(3)	1.078	1.082/−0.009
HCH	118.2(23)	114.40	115.27/−2.93
C_1GeH	108.8(12)	110.4	109.84/1.04
HC_1Ge	—	115.48	113.29/–
$C_2C_1C_3$	—	59.38	59.80/–
$C_1C_2C_3$	—	60.36	60.10/–
ω_1[c]	55.5(16)	—	52.8/−2.7
ω_2[d]	57.3(19)	—	60.5/3.2

[a] The geometry optimization used a 4–21G(C)/3–21G*(Ge) basis.
[b] Not refined parameter.
[c] Dihedral angle between line C_1—Ge and plane $C_1C_2C_3$.
[d] Dihedral angle between line C_1—H and plane $C_1C_2C_3$.
[e] In r_e units.

Dimethylgermane. The molecular structure of dimethylgermane has been determined by microwave spectroscopy.[27] The MM3-calculated structure agrees well with that observed (see Table 12). The barrier to the methyl rotation was determined as 1.18(3) kcal mol^{-1}, compared with the MM3 value of 1.23 kcal mol^{-1}. However, the dipole moment of dimethylgermane is calculated too large by MM3, 0.73 D, and 0.616(6) D from experiment.

Trimethylgermane. The molecular structure, r_s value, of trimethylgermane was determined from the rotational spectrum.[28] All three methyl groups were assumed to be the same to determine the Ge—C bond lengths and CGeC bond angles. The observed data and MM3 results are summarized in the Table 13.

Table 20. Molecular structure (r_g) of cyclobutylgermane

	Exptl[39]	MM3/Δ
Ge—C_1	1.950(4)	1.948/−0.002
Ge—H av.	1.513(8)	1.529/0.016
C_1—C_2	1.559(7)	1.559/0.000
C_2—C_3	1.560 (constrained)	1.558/–
C—H av.	1.085(4)	1.113/0.028
$C_2C_1C_4$	89.6(7)	87.7/−1.9
HCH	105.9(32)	112.1/6.5
C_1GeH(eq)	103.7(29)	107.8/4.1
(ax)	110[a]	107.8/–
ω_1[b] (eq)	25.3(31)	32.4/5.1
(ax)	20.4(36)	27.4/7.0
ω_2[c] (eq)	131.2(11)	130.2/−1.0
(ax)	126.4(19)	129.7/3.3
Moments of inertia	Exptl[40]	MM3/%
I_x (eq)	56.780	56.9611/0.32
(ax)	69.902	68.6784/−1.75
I_y (eq)	320.537	315.7213/−1.50
(ax)	281.534	289.4080/2.80
I_z (eq)	349.853	343.7174/−1.75
(ax)	298.278	306.4564/2.74

[a] Not refined.
[b] Puckering angle.
[c] The dihedral angle of the Ce—C_1 bond and $C_2C_1C_4$ plane.

Table 21. Molecular structure (r_o) of germacyclopentane

	Exptl[42]	MM3/Δ
Ge—C	1.95 (assumed)	1.963/–
Ge—H	1.53 (assumed)	1.537/–
C—C av.	1.53 (assumed)	1.539/–
C—H av.	1.09 (assumed)	1.103/–
HCH (θ_0)	109 (assumed)	107.3/–
HGeH	111 (assumed)	110.1/–
GeCC	106	103.1/−2.9
CGeC	98	93.6/−5.4
CCC	115	109.3/−5.7
Moments of inertia[a]	Exptl[42]	MM3/%
I_x	94.958	94.8787/−0.08
I_y	177.866	177.8207/0.03
I_z	247.625	247.4586/−0.07

[a] Rotational constants: A = 5323.7 MHz, B = 2842.20 MHz, C = 2041.52 MHz.

Table 22. Molecular structure (r_g) of 1-methyl-1-germaadamantane

	Exptl[46]	MM3/Δ
Ge—C av.	1.954(3)	1.947/−0.007
C—C av.	1.545(2)	1.546/0.001
C—H av.	1.112(8)	1.114/0.002
C_7GeC_9	101.8(5)	101.9/0.1
GeC_7C_1	106.3(5)	106.3/0.0
$C_1C_2C_3$	113.2(50)	113.9/0.7
$C_2C_1C_6$	107.5(15)	109.3/1.8
$\omega C_1C_2C_3C_4$	57.9	54.3/−3.6
ω[a]	120.4(12)	117.9/−2.5

[a] The angle between plane $C_1C_2C_3$ and plane $C_1C_3C_7C_8$.

Table 23. Molecular structure (r_g) of digermane

	Exptl[47]	MM3/Δ
Ge—Ge	2.403(3)	2.403/0.0
Ge—H	1.541(6)	1.535/−0.006
HGeH	106.4(8)	107.0/0.6
GeGeH	112.5(8)	111.9/−0.6

Table 24. Molecular structure of hexaphenyldigermane

	Exptl[49]	MM3/Δ
Ge—Ge	2.437(2)	2.434/−0.003
Ge—C av.	1.958	1.954/−0.004
C—C av.	1.388	1.399/0.011
GeGeC av.	110.8	110.0/−0.8
CGeC av.	108.1	109.0/0.9

Tetramethylgermane. Electron diffraction[29] was applied to determine the molecular structure of tetramethylgermane, r_g value. The methyl barrier was measured as 1.3 kcal mol^{-1} by far-infrared spectroscopy,[30] which was different from that in an earlier study, 0.65 kcal mol^{-1}.[31] The former value is consistent with the other studies of methyl-substituted germanes. MM3 gives the barrier as 1.24 kcal mol^{-1}.

Ethylgermane. Various methods have been employed in studying the structure of ethylgermane.[16,32] The experimental individual bond lengths have a large uncertainty. The moments of inertia are fitted very well although the individual bond lengths are fitted poorly. The germyl and methyl barriers were 1.41(3) and 2.85(3) kcal mol^{-1} from microwave analysis, respectively. MM3 gives values of 1.38 and 2.71 kcal mol^{-1}.

Propylgermane and methylethylgermane. Methylethylgermane and propylgermane, which would normally be used to determine the torsional parameters 1–1–1–31 and 1–1–31–1, have not been studied experimentally or theoretically yet. The *ab initio* method can be carried on our IBM workstation, but the largest basis available in Gaussian 90 is STO-3G for germanium, which would not be expected to give a good predictions of energies. However, there is a molecule, 1-methylgermacyclohexane, that we can use for parametrization. This molecule has been investigated in an NMR study.[33] From ^{14}C and ^{73}Ge chemical shift data, it was found that the axial and equatorial conformers have an equilibrium ratio of 60:40, which corresponds to the axial isomer being more stable by 0.24 kcal mol^{-1}. MM3 calculations give a value of 0.20 kcal mol^{-1} (ΔE). Applying this parameter set, we also studied methylethylgermane, propylgermane and 2-, 3- and 4-methylgermacyclohexane. Tables 16 and 17, show that the MM3 results are similar to those obtained by MM2 calculations and to those reported by Ouellette.[34] For methylgermacyclohexane, as the methyl group is shifted to the 2-, 3- and 4-positions, the effect of germanium becomes smaller and the axial–equatorial energy difference should be closer to that of cyclohexane (2.09 kcal mol^{-1}, ΔG), and the trend is shown in Table 17.

Table 25. Torsional barriers of organogermanes

Compound		Exptl	MM3/Δ
Methylgermane (Me)		1.24[26]	1.23/−0.01
Dimethylgermane (Me)		1.18(3)[27]	1.23/0.05
Trimethylgermane (Me)		—	1.24/–
Tetramethylgermane (Me)		1.3[29]	1.24/−0.06
Ethylgermane (Me)		2.85(3)[16]	2.71/−0.14
(germyl)		1.41(3)[16]	1.38/−0.03
Vinylgermane		1.238(57)[35]	1.21/−0.028
Cyclopropylgermane (germyl)		1.36[38]	1.32/−0.04
Germacyclopentane (pseudo rot.)		5.9(1)[43,a]	4.01/–
Digermane		1.49(20)[48]	1.49/0.00
Cyclobutylgermane	ΔG_{ax-eq}	0.74[39]	0.78/0.04
Barriers	ΔE_{germyl}	1.26(eq)[40]	1.23/−0.03 (eq)
		1.19(ax)[40]	1.29/0.10 (ax)
	ΔE[b]	1.24[40]	1.60/0.36

[a] See text.
[b] Barrier to interconversion of the equatorial to axial conformation.

Table 26. Dipole moments of organogermanes

Compound	Exptl	MM3/Δ
Methylgermane	0.635(6)[26]	0.64/0.00
Dimethylgermane	0.616(6)[27]	0.73/0.11
Trimethylgermane	—	0.64/–
Ethylgermane	0.76(2)[16]	0.64/−0.12
Vinylgermane	0.50(3)[35]	0.50/0.00
Germacyclopentane	0.665(7)[43]	0.70/0.03

Vinylgermane. The r_0 molecular structure has been determined by microwave studies,[35] but many structural parameters were assumed. The experimental quantities therefore contain sizable uncertainties. The MM3 geometry agrees with the experiment to within the uncertainties in the latter. The moments of inertia are well calculated (see Table 18). The MM3 structure is believed to be more reliable.

Cyclopropylgermane. The molecular structure of cyclopropylgermane has been determined by electron diffraction,[36] which gave an r_a structure. The following assumptions were made to reduce the number of the experimental structural parameters: all C—H bond lengths were equal, and Ge—H bond lengths were equal and the germyl group had local C_{3v} symmetry. A Hartee–Fock calculation was also reported.[37] The results are listed in Table 19. The rotational barrier of the germyl group is also well reproduced, 1.32 kcal mol^{-1} by MM3

compared with the experimental value of 1.36 kcal mol^{-1}.[38]

Cyclobutylgermane. There are two reports on the structure and conformations of this molecule, using electron diffraction[39] and microwave[40] methods. MM3 calculates the C—C and Ge—C bond lengths close to the experimental values, but not the Ge—H and C—H bond lengths. Since there was only one large peak in the 1.5 Å region, it was difficult to obtain accurate individual bond lengths. The 2–3 bond lengths appear to have been constrained to be too large in the experimental work, forcing the Ge—H bond to be too short. We feel that the MM3-calculated Ge—H bond length is more reliable than the experimental value. The C—H bond length for cyclobutane itself was determined to be 1.109(3) Å (an r_g value) by Kuchitsu and co-workers[41] and MM3 gives a value of 1.113 Å. For cyclobutylgermane, the C—H bond length was reported to be 1.085(4) Å, compared with 1.113 Å by MM3. There is no obvious reason for this C—H bond shortening. The four-membered ring is calculated to be slightly more puckered by MM3 than is found experimentally. The free energy difference between equatorial and axial conformers was determined experimentally to be 0.74 kcal mol^{-1},[39] and MM3 gives 0.78 kcal mol^{-1}. Also, the germyl group rotational barriers are fitted fairly well (see Table 25). Moments of inertia are poorly reproduced because of the lack of a torsion–bend interaction.[40] This error is found in all monosubstituted cyclobutanes with MM3.

Germacyclopentane. Four isotopic species of germacyclopentane have been studied by microwave spectroscopy[42] to determined the molecular structure. Even then, the structural parameters could not be determined unless the values of some parameters were assumed. Only the CGeC, CCGe, CCC and twist angles were then determined. The MM3-calculated individual parameters for this heterocyclic five-membered ring compound agree poorly with experiment, but the moments of inertia are fitted fairly well. This suggests that the constraints placed upon the experimental interpretation of the data were inadequate and we feel that the MM3 structure is better. The microwave study indicated that the C_2 half chair form was more stable than the C_s envelope form by 1.4 kcal mol^{-1}. A far-infrared study by Durig *et al.* showed that the barrier to pseudorotation in germacyclopentane was 5.9 kcal mol^{-1}.[43] The same barrier of silacyclopentane was determined to be 3.9–4.04 kcal mol^{-1}.[44] We therefore believe the value for germacyclopentane is too high. The Ge—C bond is only slightly longer than the Si—C bond, and the barrier to pseudorotation should be similar to the barrier for silacyclopentane. MM3 calculation gives the C_2 form as the most stable, and the C_s form is higher by 4.01 kcal mol^{-1}, which is the height of the pseudorotational barrier. The MM3 energy of the planar form is 5.81 kcal mol^{-1} above the C_2 form.

1-*tert*-Butylgermacyclohexane. The conformational energy of 1-*tert*-butylgermacyclohexane has been estimated from the ^{13}C and ^{73}Ge NMR spectra.[45] It was found by MM3 that the equatorial conformer is more stable by 0.62 and 1.47 kcal mol^{-1} for ΔE and ΔG, respectively. The value determined by NMR was 1.3 kcal mol^{-1} (ΔG). The MNDO method gave a value of 0.60 kcal mol^{-1} (ΔE). The earlier MM2 calculations showed an energy difference of 0.33 kcal mol^{-1} and an old molecular mechanics calculation by Ouellette[34] gave 1.23 kcal mol^{-1}.

1-Methyl-1-germaadamantane. The structure of this compound appears to have been well determined by electron diffraction.[46] The MM3 structure (Table 22) agrees with the experimental structure fairly well, except for the average Ge—C bond length, which is calculated too short by 0.007 Å. The experimental value seems well determined, and the MM3 value is thought to be less accurate for unknown reasons.

Digermane. This molecule has been studied by the electron diffraction method.[47] No spectroscopic study has been published for digermane itself, but from the IR and Raman studies of the hexaphenyl derivative in the solid, the Ge–Ge stretching mode was observed in the region of 220–250 cm^{-1}. MM3 gives a value of 225 cm^{-1} for that mode for digermane. The Ge—Ge bond length was determined to be 2.403(3) Å (r_g), compared with the Si—Si bond length, 2.331(2) Å in disilane, and the C—C bond length in ethane, 1.534(2) Å. The change in bond length on going from silicon to germanium is much smaller than the change on going from carbon to silicon, as expected. MM3 calculated the Ge—Ge bond length to be 2.403 Å. The GeH_3 barrier was determined to be 1.49(20) kcal mol^{-1},[48] and MM3 also gives 1.49 kcal mol^{-1} (ΔE).

Hexaphenyldigermane. The molecular structure of hexaphenyldigermane has been determined using x-ray crystallography.[49] The solid-phase IR and Raman spectra were also recorded. The GeGeC bending frequencies were found around 200 cm^{-1}, and were used to determine the GeGeC force constant. The Ge—Ge bond length is stretched out to 2.434 Å by MM3 calculation, in agreement with the experimental value of 2.437(2) Å. The CGeC and GeGeC angles are 109.0 and 110.0° as given by MM3, compared with the experimental values of 108.1 and 110.8°, respectively.

Heats of formation

The heats of formation for molecules of this class were

Table 27. Heats of formation of germanes[a]

Compound	*W*	$H_f°$	SumH	Steric	Pop	TORS	T/R	Calc./Δ
Tetraethylgermane	5	−34.6(1.2)	−77.83	6.63	0.0	1.68	2.40	−34.73/−0.14
Tetra-*n*-propylgermane	5	−54.9(1.0)	−104.76	10.65	1.2	3.36	2.40	−54.90/0.13
Hexaethyldigermane	5	−75.5(2.2)	−116.75	−9.13	0.0	2.94	2.40	−75.50/0.00

Best values:
Ge—C = 8.0962 Ge—Ge = −3.5375
Standard deviation = 0.11

[a] *W* = Weight.

also calculated using the usual method.[50] Unfortunately, there are very limited data available, for tetraethylgermane, tetra-*n*-propylgermane and hexaethyldigermane. Additionally, the experimental data[51] have fairly large errors (1.5 kcal mol^{-1} on average). They are all fitted fairly well, but the small standard deviation (0.106 kcal mol^{-1}) is a result of the limited data. Only two parameters were derived, the bond increments of C—Ge and Ge—Ge. The Ge—H bond increment and structural features are missing because no data for molecules containing these moieties have been reported. The MM3 results are summarized in Table 27. We would expect that heats of formation can be calculated for tetraalkylgermanes and hexaalkyldigermanes with an expected error of about 2 kcal mol^{-1}.

Parameterization

A reviewer asked that we outline just how the parameterization was done in the work described here. We will try to give here sufficient detail so that the process could be repeated by someone knowledgeable in molecular mechanics and in each of the experimental methods discussed.

The standard procedure for fitting parameters to data is to use the least-squares method, and weight the data proportionally to the inverse of their experimental errors.[52] We tried to do this long ago,[53] but found that, generally, much better results could be obtained in the following way. One needs to start with a trial set of parameters. These can now be conveniently obtained from the MM3 program itself.[54] Lacking that, one simply needs to guess some approximate numbers (estimates of bond lengths, angles, stretching and bending constants and the like). One then carries out geometry optimization calculations on all of the molecules in the data set, and examines the results. For the most part, the results should be within the 'ballpark.' That is, the bond lengths may be in error by 0.03 Å, the angles by 5–10°, etc., but at least one has an approximate structure for each molecule, an initial estimate of the vibrational spectrum ($\pm$ 100 cm^{-1}) and approximate parameters. The point is to then refine the parameters so as to reproduce overall the structures and other available data as well as possible. The reason why a brute-force type least-squares fit is generally not very good is that one usually does not have reliable estimates of the experimental errors, and therefore cannot reliably weight the terms that go into the fitting. Some reasons why the experimental errors are not accurate include the fact that the experimental data may span a time period of up to 50 years or so. Many kinds of systematic errors were uncovered, and gradually reduced over that period. Since the measurements come from many different laboratories, one does not know when various improvements were incorporated in a given laboratory, and therefore there is no straightforward way to allow for this chronological effect in weighting the data. At least two other major problems arise. The most important of these is that when electron diffraction, x-ray, neutron diffraction or microwave data are being fitted by the experimentalists in the derivation of the structure, one determines an 'estimated standard deviation' in the structural parameters. This is a measure of how well the structure fits the data, but frequently not a measure of how accurate the structure is. The problem is that different structures may equally well fit the data. For example, a radial distribution peak may be made up of two Gaussian peaks, each of which has some half bandwidth. It is not possible from this experimental information alone to determine if those two lines are farther apart with relatively small vibrational amplitudes, or closer together with large vibrational amplitudes. However, what one can do is to measure the average of the two with good accuracy. In comparing with experiment then, one may find one molecular mechanics bond length is too long relative to experiment, and another is too short, but the average is just right. This probably means that the molecular mechanics values are correct. The individual experimental values are often not accurate, but the average is (which is what is actually measured). Consequently, such reported individual bond lengths need to be given minimal weight in this case.

Microwave data are difficult to interpret in another way. If one has enough isotopic data, then one can generate an r_S structure. However, the relationship between the r_S structure and any other kind of structure (e.g. the r_g structure obtained from electron diffraction) was not known until recently.[24a] If an r_o or r_z structure is obtained instead, the rotational frequencies upon which

this structure is based are usually accurate to five or six decimal places. However, normally one has to assume various things about the molecule in order to be able to solve the structure. Thus the accuracy of the structure obtained is highly dependent upon these assumptions, regardless of the accuracy to which the rotational frequencies are measured. Finally, it is now pretty clear just what the differences are between r_e, r_g, r_α, r_s, etc. structures, and it is possible to interconvert them fairly accurately (see Ref. 24 and references cited therein). Some of these interconversions have been understood for many years,[55] but some have not.[24b] We have always fitted MM2 and later force field structures to r_g. If the experimental structure is something else, an interconversion must be made before they can be compared.

X-ray data are especially problematic. X-rays are scattered by electrons, not by nuclei. Hence x-rays measure positions of electron density, not nuclear positions, and the structure is found as it exists in the crystal lattice. The structure in the lattice may be similar to that of the isolated molecule, or it may not, and it is often found that an accurate structure for the isolated molecule cannot be found from the available data.

Thermal motion is also a major problem in the interpretation of x-ray data. Bond lengths are commonly measured too short by x-ray methods by up to 0.015 Å from this effect, if the measurements are made at room temperature. Coupled with the problem that x-rays measure electron density positions rather than nuclear positions, the 'atomic positions' are often misplaced relative to the nuclear positions by as much as 0.03 Å in routine crystallographic studies. Obviously errors of this size are a disaster in force field calculations. Although these things are well understood, they are not widely understood, and they are often dealt with poorly in the existing literature.

Accordingly, rather than to try formally to weight the data, in most cases we simply examined the calculated structures and compared them with the experimental structures. There usually appear to be errors, but when one considers the individual apparent errors with respect to the kinds of things that are discussed above, one can reach a conclusion about the 'weight' that should be applied to that particular information. Hence this 'weighting' is not done in a programmed way, but is based upon the experience of the person doing the weighting on a case by case basis. One might argue that one should actually have a rigorous programmed method for carrying out this weighting, so as to make it reproducible. However, this is rather like saying that our legal system should be sufficiently detailed so that it always works. (Experience has shown that as time passes, the legal system becomes increasingly complex, forbiddingly so in fact, but there is no indication that it is working any better than it did previously.)

In the 1970s we in fact tried to automate these procedures so that all of these things would be taken care of in a programmed way. We were not able to do this at all well, and eventually concluded that the system which we used, and still use, is really the best that can be done, for the most part. It should be pointed out that we work with relatively limited data sets, where the data come from a variety of sources and experimental techniques, so that one does not mentally have to process very many numbers. Also, the data sets are highly redundant. One wants to make sure that one fits 'independent' data. However, often the same information is obtained repeatedly from additional molecules, so that additional data are redundant data, and they are of no help.

The above is not as straightforward as it may seem. The problem is that often one does not know (exactly) what the force field should be like, that is to say, what kinds of terms should be present in the force field equations, when one is carrying out the parameterization. Hence the parameters are adjusted to fit the data, with the assumption that the force field itself is adequate. That means that errors in the force field from omitting significant terms are taken up in the parameterization of other terms. Depending on the importance of what terms were left out, a cascade of problems may result. Nevertheless, the whole procedure works fairly well (to some approximation), so that even a diagonal quadratic force field like MM2 (which Hagler and co-workers refer to as Class 1[56]) will give a reasonable fit to most of the data (other than vibrational spectra, and even those are roughly correct). Class 2 and Class 3 force fields do better (Class 2 force fields contain off-diagonal elements and anharmonic terms, whereas Class 3 force fields allow specifically for chemical effects). MM3 is a rather minimal Class 3 force field.[3] That is, it is known from more detailed studies on various classes of compounds that certain cross-terms left out of MM3 limit the accuracy of the spectroscopic calculations.[57] However, MM3 contains only a few specific well defined cross-terms, so that what is really needed to improve the frequency calculations is not part of MM3.

Some parts of these calculations have in fact been highly automated. For example, in the calculation of heats of formation, one usually has a sizable body of data where the accuracies of the measurements are indeed known. Therefore, one can apply standard least-squares methods with reasonable confidence. Of course, there are always outliers in any such statistical procedure, and one must decide how they will be handled on an individual basis.

The use of quantum mechanical data greatly facilitates force field parameterization, but it comes with its own set of problems. The most difficult part of the force field parameterization from experimental data has usually been to find the appropriate torsional potentials. These can more readily be determined from quantum mechanical calculations than from experiments. However, the accuracy of these terms is more or less sensitive to the size of the basis set used for the calculation, the amount

of correlation included in the calculation and the type of structure involved. For saturated hydrocarbons, it is known that to obtain a 'converged' result for the torsional potential, one needs to include triple zeta (but not quadruple zeta or higher) basis functions, and one needs to include d orbitals (but no f orbitals). Anything less than complete correlation is suspect.[58] However, this is only for a hydrocarbon. It may be reasonably presumed that for functionalized molecules higher levels of calculation will be needed, but just how high is something that will still have to be determined for individual classes of compounds. Such studies have not yet been reported in the literature, and they may not be as straightforward as is often assumed.[59] Then, of course, the r_e structure obtained in this way has to be converted to whatever kind of experimental structure is used for comparison. The literature abounds with statements such as 'the molecular mechanics C—H bond lengths do not agree with the *ab initio* values' and the differences are large (about 0.03 Å). However the agreement is in fact excellent when the r_e value is converted to r_g before the comparison is made (less than 0.01 Å). The error is not in the calculations, but in the comparison of quantities that are not comparable.

With systems that are reasonably complicated, it can be non-trivial to determine torsional potentials, even having adequate quantum mechanical data. If we have a system in which there are tetrahedral atoms on both ends of a bond, and we consider rotation about that bond, if all of the substituents are different, then we need torsion potentials for nine different atom pairs, and these potentials must contain at a minimum V_1, V_2 and V_3 terms (a total of 27 parameters). One rarely (probably never) has that much information. Fortunately, in practice one usually has a much smaller number of interactions to consider. Nonetheless, if one has these kinds of data for several molecules, then determining all of the torsion parameters can be a formidable job. Programs that utilize least-squares methods have been written to assist in this process (e.g. TORSFIND[60]). It is sometimes difficult to be certain that one has arrived at a unique fit, or even a generally acceptable fit*. One has to work with those data that are available.

This is an outline of the scheme that we applied in the present case, and that we generally apply, in developing a parameter set for a new class of compounds. Heats of formation are normally fairly useful in uncovering errors that otherwise would slip by†, but in the present case insufficient such data are available to be useful.

The test then is how well the force field fits the data‡. All of the constants determined in the present work are given, together with all of the data calculated with MM3 using these constants, and the corresponding experiments to which they were fitted. Any of this can be checked by carrying out the calculations and obtaining the results. In our judgment, this is the best fit that we are able to obtain from this force field for these data. Often in the past someone has been interested in a small subset of compounds, and has observed that by changing a few constants, that subset could be fitted more accurately. Normally such changes introduce very large errors and unwanted results in various other places, however, so that a force field based on limited information is a very dangerous thing§. We do not recommend this procedure. On the other hand, if one wishes to change some of the parameters, and then reoptimize the entire data set here, the results will indeed change. Some may be better, and some worse. Which set is better may be a matter of judgment. In our judgment, we have chosen the optimum parameter set, based on the available data cited here.

CONCLUSIONS

This MM3 study shows that organogermanes can be treated essentially like hydrocarbons, and the accuracy of the results are of 'experimental accuracy' (except for spectra). The vibrational spectra of nine compounds were reasonably reproduced with an r.m.s. error of 42 cm^{-1}, which is similar to that for hydrocarbons (35 cm^{-1}). The molecular structures of 13 organogermanes were calculated family well by MM3. The moments of inertia were also fitted well to experimental data, mostly, within $\pm$ 0.5% except cyclobutylgermane. This error can be fixed by inclusion of torsion–bend interaction (which is available in MM4, but is not part of the MM3 force field). The rotational barriers and conformational energies are adequately calculated.

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* In fact, unique fits are the exception rather than the rule. There may be more adjustable parameters than data, so the best one can do is to pick a parameter set that fits the data, and that seems physically reasonable. Automatic procedures sometimes give torsional constants of dozens (or more) of kcal mol^{-1}, where the observables are small differences between large numbers. These usually have to be discarded as physically unreasonable, even though they may fit the data.

† Because they can give many data points to fit with few adjustable parameters, they apply constraints so that errors imposed by other parts of the force field may then become obvious.

‡ What we really would like to know is how well the force field will predict unknown structures. We cannot know that with certainty, but if the data used in the parameterization are highly diverse, then the accuracy of the fit to those data will probably approximate the reliability applied to other structures. In a sense the force field is a fancy interpolation scheme. However, if it is used for an extrapolation (for example, if one is making a prediction regarding a bond angle that is far more bent than any known angles in the data set), then the accuracy is suspect. Hence the force field has limits, but some of these limits may not be well defined or even recognized.

§ It corresponds to having far more adjustable parameters than data. Obviously the data can indeed be well fitted. Such a force field, however, is probably going to be generally useless, or worse.

REFERENCES

1. The MM2 and MM3 programs are available to all users from Tripos Associates, 1699 South Hanley Road, St Louis, MO 63144, USA and to academic users only from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 47405, USA.
2. N. L. Allinger, M. I. Quinn, K. Chen, B. Thompson and M. R. Frierson, *J. Mol. Struct.* **194**, 1 (1989).
3. (a) N. L. Allinger, Y. H. Yuh and J.-H. Lii, *J. Am. Chem. Soc.* **111**, 8551 (1989); (b) J.-H. Lii and N. L. Allinger, *J. Am. Chem. Soc.* **111**, 8566 (1989); (c) J.-H. Lii and N. L. Allinger, *J. Am. Chem. Soc.* **111**, 8576 (1989).
4. N. L. Allinger, F. Li and L. Yan, *J. Comput. Chem.*, **11**, 848 (1990).
5. N. L. Allinger, M. R. Rahman and J.-H. Lii, *J. Am. Chem. Soc.* **112**, 8293 (1990).
6. N. L. Allinger, K. Chen, M. Rahman and A. Pathiaseril, *J. Am. Chem. Soc.* **113**, 4505 (1991).
7. L. R. Schmitz and N. L. Allinger, *J. Am. Chem. Soc.* **112**, 8307 (1990).
8. N. L. Allinger, F. Li, L. Yan and J. C. Tai, *J. Comput. Chem.* **11**, 868 (1990).
9. N. L. Allinger, J. Kuang and H. Thomas, *J. Mol. Struct. (Theochem).* **209**, 125 (1990).
10. N. L. Allinger, M. I. Quinn, M. Rahman and K. Chen, *J. Phys. Org. Chem.* **4**, 647–658 (1991).
11. K. Chen and N. L. Allinger, *J. Phys. Org. Chem.* **4**, 659–666 (1991).
12. N. L. Allinger, S. Rodriguez and K. Chen, *J. Mol. Struct. (Theochem)* **260**, 161 (1992).
13. H. W. Kattenberg, W. Gabes and A. Oskam, *J. Mol. Spectrosc.* **44**, 425 (1972).
14. G. R. Wilkinson and M. K. Wilson, *J. Chem. Phys.* **44**, 3867 (1966).
15. J. E. Griffiths, *J. Chem. Phys.* **38**, 2879 (1963).
16. J. R. Durig, A. D. Lopata and P. Groner, *J. Chem. Phys.* **66**, 1888 (1977).
17. K. M. Mackay and R. Watt, *Spectrochim. Acta, Part A*, **23**, 2761 (1967).
18. Y. Imai and K. Aida, *Bull. Chem. Soc. Jpn.* **54**, 3323 (1981).
19. J. R. Durig and J. B. Turner, *Spectrochim. Acta. Part A* **27**, 1623 (1971).
20. J. R. Durig and J. N. Willis, Jr, *J. Chem. Phys.* **52**, 6108 (1970).
21. J. R. Durig, C. W. Sink and J. B. Turner, *J. Chem. Phys.* **49**, 3422 (1968).
22. J. R. Durig, T. S. Little, T. J. Geyer and M. Dakkouri, *J. Phys. Chem.* **93**, 6296 (1989).
23. H. D. Thomas, K. Chen and N. L. Allinger, *J. Am. Chem. Soc.* **116**, 5887 (1994).
24. (a) B. Ma and N. L. Allinger, *J. Mol. Struct.* **414**, 395 (1997); (b) B. Ma, J.-H. Lii, H. F. Schaefer and N. L. Allinger, *J. Phys. Chem.* **100**, 8763 (1996); (c) B. Ma, J.-H. Lii, K.-H. Chen and N. L. Allinger, *J. Am. Chem. Soc.* **119**, 2570 (1997).
25. W. A. Kreiner, R. Opferkuch, A. G. Robiette and P. H. Turner, *J. Mol. Spectrosc.* **85**, 442 (1981).
26. V. W. Laurie, *J. Chem. Phys.* **30**, 1210 (1959).
27. E. C. Thomas and V. W. Laurie, *J. Chem. Phys.* **50**, 3512 (1969).
28. J. R. Durig, M. M. Chen, Y. S. Li and J. B. Turner, *J. Phys. Chem.* **77**, 227 (1973).
29. J. L. Hencher and F. J. Mustoe, *Can. J. Chem.* **53**, 3542 (1975).
30. J. R. Durig, S. M. Craven and J. Bragin, *J. Chem. Phys.* **52**, 2046 (1970).
31. G. W. Smith, *J. Chem. Phys.* **42**, 4229 (1965).
32. J. R. Durig and C. W. Hawley, *J. Phys. Chem.* **75**, 3993 (1971).
33. (a) Y. Takeuchi, M. Shimoda, K. Tanaka, S. Tomoda, K. Ogawa and H. Suzuki, *J. Chem. Soc., Perkin Trans. 2*, 17 (1988); (b) Y. Takeuchi, M. Shimoda and S. Tomoda, *Magn. Reson. Chem.* **23**, 580 (1985).
34. R. J. Ouellette, *J. Am. Chem. Soc.* **94**, 7674 (1972).
35. J. R. Durig, K. L. Kizer and Y. S. Li, *J. Am. Chem. Soc.* **96**, 7400 (1974).
36. M. Dakkouri, *J. Am. Chem. Soc.* **113**, 7109 (1991).
37. (a) W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. DeFrees, J. A. Pople and J. S. Binkley, *J. Am. Chem. Soc.* **104**, 5039 (1982); (b) K. D. Dobbs and W. J. Hehre, *J. Comput. Chem.* **7**, 359 (1986).
38. M. B. Kelly, J. Laane and M. Dakkouri, *J. Mol. Spectrosc.* **137**, 82 (1989).
39. M. Dakkouri, *J. Mol. Struct.* **130**, 289 (1985).
40. J. R. Durig, T. J. Geyer, P. Groner and M. Dakkouri, *Chem. Phys.* **125**, 299 (1988).
41. T. Egawa, T. Fukugama, S. Yamamoto, F. Takabayashi, H. Kambara, T. Ueda and K. Kuchitsu, *J. Chem. Phys.* **86**, 6018 (1987).
42. E. C. Thomas and V. W. Laurie, *J. Chem. Phys.* **51**, 4327 (1969).
43. J. R. Durig and J. N. Willis Jr, *J. Chem. Phys.* **52**, 6108 (1970).
44. (a) J. R. Durig and J. N. Willis Jr, *J. Mol. Spectrosc.* **31**, 320 (1969); (b) J. Laane, *J. Chem. Phys.* **50**, 1946 (1969).
45. Y. Takeuchi, T. Tanaka, T. Harazono and S. Yoshimura, *Bull. Chem. Soc. Jpn.* **63**, 708 (1990).
46. Q. Shen, C. A. Kapfer, P. Boudjouk and R. L. Hilderbrandt, *J. Mol. Struct.* **54**, 295 (1979).
47. B. Beagley and J. J. Monaghan, *Trans. Faraday Soc.* **66**, 2745 (1970).
48. J. E. Griffiths and G. E. Walrafen, *J. Chem. Phys.* **40**, 321 (1967).
49. V. M. Drager and L. Ross, *Z. Anorg. Chem.* **460**, 207 (1980).
50. U. Burkert and N. L. Allinger, *Molecular Mechanics*. American Chemcal Society, Washington, DC (1982).
51. J. D. Cox and C. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*. Academic Press, London (1970).
52. S. Lifson and A. Warshel, *J. Chem. Phys.* **49**, 5116 (1968).
53. D. H. Wertz and N. L. Allinger, *Tetrahedron* **35**, 3 (1979).
54. N. L. Allinger, X. Zhou and J. Bergsma, *J. Mol. Struct. (Theochem)* **312**, 69 (1994).
55. K. Kuchitsu and S. J. Cyvin, in *Molecular Structures and Vibrations*, edited by S. J. Cyvin, Elsevier, New York, 1972.
56. M. J. Hwang, T. P. Stockfisch and A. T. Hagler, *J. Am. Chem. Soc.* **116**, 2515 (1994).
57. N. L. Allinger, K. Chen and J.-H. Lii, *J. Comput. Chem.* **17**, 642 (1996), and subsequent papers.
58. N. L. Allinger, J. T. Fermann, W. D. Allen and H. F. Schaefer, III, *J. Chem. Phys.* **106**, 5143 (1997).
59. See, for example, the paper How reliable are *ab initio* calculations, H.-G. Mack and H. Oberhammer, *J. Mol. Struct.* **258**, 197 (1992), and references edited therein.
60. TORSFIND is an unpublished least-squares program written by Drs Y. H. Yuh and J.-H. Lii for finding MM3 or MM4 torsional parameters from experimental or *ab initio* data from one or several compounds, and is the program that we use most of the time; Other similar programs exist, e.g. PARTS. G. Liang, P. C. Fox and J. P. Bowen, *J. Comput. Chem.* **17**, 940 (1996).