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Molecules with T Symmetry. Conformational Analysis of Systems of Type $M[C(CH_3)_3]_4$ and $M[Si(CH_3)_3]_4$ by the Empirical Force Field Method

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Abstract: Empirical force field calculations have shown that compounds of the type $M[C(CH_3)_3]_4$ and $M[Si(CH_3)_3]_4$, where M is an element of group 4A, exist in at least two conformational states: a ground state with T symmetry, and a higher energy conformer with S_4 symmetry. In addition, a C_2 form has been found for $C[C(CH_3)_3]_4$ (**2**). The energy gap between the T and S_4 forms increases with a decrease in the central M–C or M–Si bond length, and reaches a maximum of 16 kcal/mol for the most strained member of the series, **2**.

The symmetry of every molecule—properly speaking, of every molecular model—under the rigid body approximation may be described by some point group, and that of a chiral molecule by one of five: C_n, D_n, T, O, and I. Curiously, whereas molecules with C_n or D_n symmetry are commonplace,[1] chemical representatives of the remaining three groups are generally considered to be unknown.[2] This state of affairs is rendered the more remarkable by the fact that T, O, and I are the pure rotation groups of the well-represented achiral tetrahedral (T_d and T_h),[4] octahedral (O_h),[5] and icosahedral (I_h)[6] groups, respectively.

Chemical structures belonging to one of these chiral groups are readily envisaged: it is merely necessary to combine an achiral skeleton of the appropriate symmetry with a set of ligands which preserves all symmetry elements of the first kind while destroying all those of the second.[7] This principle underlies the elaborate design of various hypothetical molecules with T[1,8] and O[9] symmetry.[10] Over 30 years ago, Herzberg,[11] applying the same principle, pointed out that T symmetry is exhibited by any conformation of neopentane, $C(CH_3)_4$, in which each methyl group is twisted in the same sense and to the same extent ($0 < \phi < \pi/3$) relative to a T_d conformation ($\phi = 0$ or $\pi/3$).[12] The present paper is devoted to a fuller exploration of Herzberg's appealingly simple idea by an examination of conformational preferences in molecules of the type MR_4, where M is an element of group 4A and R = $C(CH_3)_3$ or $Si(CH_3)_3$.

Symmetry and Time Scale. Central to the definition of molecular symmetry is the time scale of measurement to which the symmetry refers. In discussing nonrigid molecules which can undergo internal torsional motion, such as neopentane and molecules of the type MR_4, it is therefore essential to specify the particular model of the molecule which is appropriate to

the conditions of measurement. The symmetry label attached to that model is then a fair expression of "molecular symmetry" under the stated conditions.[13]

For nonrigid molecules the appropriate group is the Longuet-Higgins molecular symmetry (MS) group,[14] which may be conveniently expressed as the semidirect product of the torsional subgroup of the ligands and the frame subgroup of the skeleton.[15] In the context of the present discussion, it is instructive to examine the case of a molecule of the type CR^*_4, where R^* is an asymmetric ligand and all four ligands have the same absolute configuration.[16] The highest point group symmetry possible for such a molecule is D_2,[1] and all conformations of CR^*_4 must therefore belong to D_2 or to one of its subsymmetries (i.e., C_2 or C_1). However, we might be dealing with a nonrigid molecule, and the appropriate symmetry group in that case is the MS group, with feasible transformations corresponding to the internal motions of the molecule. The molecular symmetry group is therefore $(C_1)^4 \wedge T$, a group of order 12 which is isomorphic to T. In other words, the symmetry of time-averaged CR^*_4 is *permutationally equivalent to T.*[17]

Similarly, seen as a rigid structure, neopentane has T_d symmetry in the ground state.[18] On the other hand, viewed as a structure in which internal rotations of the methyl groups are time averaged, the molecular symmetry group of neopentane[15] is $(C_3)^4 \wedge T_d$, of order 1944. Evidently, Herzberg's T symmetry for neopentane refers to a molecule frozen into a conformation which is unstable relative to the T_d ground state.

Static and Dynamic Symmetry of Tetrakis(trimethylsilyl)-silane (1). In 1970 an electron diffraction study by Bartell et al.[19] showed that $Si[Si(CH_3)_3]_4$ (**1**), a silicon analogue of the unknown $C[C(CH_3)_3]_4$, exhibits T symmetry in the gas phase. Bartell et al. suggested that the deformation from T_d symmetry

Table I. Geometric Parameters Calculated for Structures of Type $M[Si(CH_3)_3]_4{}^a$

	M = C		M = Si[b]	
	T	S_4	*T*	S_4
r(M–Si), Å	1.916	1.923	2.346	2.356
r(Si–C_m), Å	1.876	1.876	1.869	1.869
θ(Si–M–Si), deg[c]	109.5	106.7 (2)	109.5	107.6 (2)
		110.9 (4)		110.5 (4)
$\theta(C_m$–Si–$C_m)$, deg	104.0	103.1	109.0	108.1
θ(M–Si–$C_m)$, deg	114.5	115.3	109.9	110.8
$\Delta\phi$, deg[d]	16.0	14.3, 12.5	15.4	12.7, 12.6
		–14.5, –13.0		–12.9, –12.4
$\Delta E_T(S_4$–$T)$, kcal/mol[e]		9.64		4.08

[a] C_m = methyl carbon. [b] See ref 20 for partial listing of structural parameters for this molecule. [c] The two listed valence angles refer to the two sets of symmetry equivalent angles in S_4 symmetry. The value in parentheses gives the number of angles in each set. [d] Deviation of the SiMe₃ groups from an ideally staggered conformation defined as $\phi(C_m$–Si–M–Si) = 60.0°. The deviation is taken as positive if a clockwise rotation of the front group is required to reach a staggered conformation. For S_4 symmetry, there are two oppositely signed sets of symmetry equivalent dihedral angles. [e] Difference in total steric energy between the S_4 and T forms, where E_T, the total steric energy, is defined in eq 1 of ref 35.

was the result of torsional displacements (by about 14°) induced by nonbonded interactions between methyl groups, and they supported their conclusion by simplified force field calculations. We recently confirmed these results, using an empirical force field especially developed for the conformational analysis of polysilanes.[20] Moreover, a search of the hypersurface of **1** disclosed a second minimum, corresponding to the S_4 form of **1**. In this conformer, which is 4.08 kcal/mol more strained than the T ground state, two of the trimethylsilyl groups are twisted away from the all-staggered T_d structure by +12.7 and +12.6°, while the other two are twisted in the opposite sense to the same extent (–12.9 and –12.4°).

If we assume rapid internal rotation of the 4 trimethylsilyl and 12 methyl groups in **1**, the molecular symmetry group of the time-averaged structure is $((C_3)^3 \wedge C_3)^4 \wedge T_d$, of order $(3^3 \times 3)^4 \times 24 = 1\ 033\ 121\ 304$. The same group describes the time-averaged structure of all members of the MR₄ series (as defined above).

The MR₄ Family. To our knowledge, **1** is the only organic molecule for which T symmetry has been found in the ground state.[21] The present work was undertaken in an effort to discover the extent to which this finding could be extended to other members of the MR₄ family, and to study the effect of structure in this series of compounds on the energy gap (ΔE_T) separating the T and S_4 conformations. Since the achiral S_4 form represents one possible intermediate in the enantiomerization itinerary of the chiral T conformers, a trend in the values of ΔE_T might suggest a parallel trend in the stability of the T form toward racemization.

To the best of our knowledge, no compounds of the type $M[C(CH_3)_3]_4$ have been reported. On the other hand, representatives of the class $M[Si(CH_3)_3]_4$ are well known, with M = C,[22] Si,[23,19] Ge,[24] and Sn;[24] higher homologues have also been reported.[25] All of these compounds exhibit the high melting points characteristic of quasi-spherical molecules,[26] but, with the single exception of **1**, their molecular structures are unknown.

Methods and Results

All structures were calculated by the empirical force field (EFF) method. Only two compounds in the series

$M[Si(CH_3)_3]_4$ were investigated, with M = C and Si. For the first we employed Allinger's 1971 force field,[27] enriched by his Si parameters,[28] and for the second we used the polysilane force field.[20] Results are given in Table I.

The $M[C(CH_3)_3]_4$ family was investigated more extensively. The first member of the series, $C[C(CH_3)_3]_4$ (**2**), was used as a test case to compare several force fields in current use. The results are given in Table II and are discussed below. Other members of the series were calculated using parameters formulated by Allinger (M = Si)[27,28] and Ouellette (M = Ge and Sn).[29,30] The parameters for germanium and tin rest on a small data base, and have not been extensively tested;[31] furthermore, because of the paucity of appropriate structural data for molecules containing Pb, parametrization for this element is all but precluded.[29] We therefore resorted to a stratagem for $M[C(CH_3)_3]_4$ which has been previously employed in studies of homologues of trimesitylmethane[33] and hexaphenylethane,[34] in which the central atom was simulated by a "carbon" atom with variable "preferred" input M–C bond lengths ($r°$) appropriate to the various group 4A atoms M. These values of $r°$ correspond to the energy minima in the harmonic potential function used to approximate bond stretching forces. In the case of carbon, this value is substantially below the equilibrium C–C bond length, r_e, but for the higher elements, it may be assumed that the larger central M–C bond distance decreases cross-bond repulsive nonbonded interactions sufficiently so that $r°$ is approximated by r_e. All other parameters for the simulated atom remain those for carbon.[27] The principal underlying assumption for this model is that the geometries and relative strain energies for such molecules are determined primarily by the steric interactions of the bulky *tert*-butyl groups, i.e., that the severity of these interactions is closely approximated by a function of the central bond distance, and that the nature of the central atom itself plays a secondary role. The justification for this starkly simple model is found in the success of its application to other classes of crowded molecules,[33,34] and in the good agreement between simulated and nonsimulated $M[C(CH_3)_3]_4$, M = Si and Ge. This method also allows calculation of structures with intermediate M–C bond lengths. Results are given in Tables III and IV and are further discussed below.

Calculations were carried out as previously described,[35] with input structures[36] optimized by the pattern search minimization technique. The recommended[35] energy criterion for terminating the minimization loop, a decrease of less than 0.01 kcal/mol over one iteration, though generally adequate, may on occasion lead to difficulties if the torsional potential is very shallow; the search may then be perceived as having ended short of the true minimum. Accordingly, in every calculation a structure with torsional angles "on the other side" of the supposed minimum was also input and optimized. A structure was considered at the energy minimum only if it was obtained by this process of optimization "from both sides".[37,39] The full relaxation technique was used and all structures were optimized without any symmetry constraints.

Discussion

Reliability of the Method. As a test of confidence in structures calculated by the EFF method, one may gauge the closeness of the match between a structure calculated by this method and the same structure as determined by conventional physical means (e.g., diffraction methods). In the present study, only one such comparison is possible, that for **1** where the agreement between calculated[20] and experimentally determined[19] structures is excellent. To augment the level of confidence, we felt it desirable to test the dependence of calculated structures on the choice of force fields. Accordingly, the structure of **2** was calculated by three different force fields in current use: Allinger's (1971),[27] Schleyer's,[40] and Bartell's

Table II. Geometric Parameters Calculated for $C[C(CH_3)_3]_4$ by Several Force Fields[a]

| | Allinger (1971)[b] | | | Schleyer[c] | | Bartell (MUB-2)[d] |
	T	S_4	C_2	T	S_4	T
$r(C_c-C)$, Å	1.628	1.634	1.628, 1.636[e]	1.640	1.644	1.668
$r(C-C_m)$, Å	1.566	1.568	1.568	1.554	1.554	1.552
$\theta(C-C_c-C)$, deg	109.5	104.5 (2)	116.5 (2)[f]	109.5	106.8 (2)	109.5
		112.0 (4)	106.1 (4)[f]		110.8 (4)	
$\theta(C_m-C-C_m)$, deg	99.3	99.0	99.9	99.5	99.1	103.3
$\theta(C_m-C-C_c)$, deg	118.3	118.6	118.2	118.2	118.7	115.1
$\Delta\phi$, deg	14.7	14.6, 14.0	3.9, 3.9	14.0	13.6, 12.9	16.6
		−15.3, −11.1	−23.0, −22.7		−14.9, −10.2	
$\Delta E_T(S_4-T)$, kcal/mol		15.99	(14.33)[g]		14.02	

[a] See Table I for explanation of parameters. C_c = central carbon atom. [b] Reference 27. [c] Reference 40. [d] Reference 43. [e] The smaller value of r refers to the bonds joining the t-Bu groups with $\Delta\phi$ 3.9°, and the larger to those with $\Delta\phi$ −23°. [f] Average values (see text). [g] $\Delta E_T(C_2-T)$.

Table III. Simulated and Nonsimulated Structures of $M[C(CH_3)_3]_4$, M = Si and Ge[a]

| | $Si[C(CH_3)_3]_4$ | | | | $Ge[C(CH_3)_3]_4$ | | | |
| | Nonsimulated[b] | | Simulated[c] | | Nonsimulated[d] | | Simulated[e] | |
	T	S_4	T	S_4	T	S_4	T	S_4
$r(M-C)$, Å	1.951	1.960	1.929	1.938	2.029	2.038	1.999	2.007
$r(C-C)$, Å	1.541	1.543	1.543	1.546	1.544	1.545	1.540	1.542
$\theta(C-M-C)$, deg	109.5	107.9 (2)	109.5	106.8 (2)	109.5	107.5 (2)	109.5	107.2 (2)
		110.3 (4)		110.4 (4)		110.4 (4)		110.6 (4)
$\theta(C-C-C)$, deg	104.8	104.2	104.3	103.7	105.8	105.3	105.4	104.8
$\theta(M-C-C)$, deg	113.8	114.3	114.2	114.8	112.9	113.4	113.3	113.9
$\Delta\phi$, deg	14.6	13.2, 13.1	14.7	13.3, 12.6	14.6	14.2, 12.6	14.6	13.6, 12.5
		−14.3, −14.1		−14.3, −14.1		−14.5, −13.4		−15.4, −13.8
$\Delta E_T(S_4-T)$, kcal/mol		11.29		11.26		9.94		10.13

[a] See Table I for explanation of structural parameters. [b] See ref 28 for silicon parameters. [c] A value of $r° = 1.87$ Å was used for the "preferred" input Si–C bond length. [d] See ref 29 for germanium parameters. [e] A value of $r° = 1.95$ Å was used for the "preferred" input Ge–C bond length.

(MUB-2).[43] As seen from the comparison in Table II, all three force fields give ground state structures with T symmetry, and all three give calculated structural parameters (bond lengths, valence angles, and dihedral angles) which are in fair agreement with each other.[44] Discussion of the S_4 and C_2 conformers is deferred to subsequent sections.

To test the reliability of the simulation procedure employed to calculate structures of higher homologues of 2 (Table IV), a comparison was made between the structures calculated for $M[C(CH_3)_3]_4$, M = Si and Ge, by use of the appropriately parametrized force field,[28,29] and by the simulation procedure using $r° = 1.87$ and 1.95 Å, respectively (Table III). With the exception of the M–C bond, all parameters, notably $\Delta\phi$ and ΔE_T, are reproduced with considerable accuracy for both the T ground state and the higher energy S_4 conformation. The shorter simulated M–C bond length is not unexpected, since the bond stretching force constant for a carbon–carbon bond $(4.40 \text{ mdyn}/\text{Å})^{27}$ is somewhat higher than for a silicon–carbon $(2.92 \text{ mdyn}/\text{Å})^{28}$ or germanium–carbon bond $(2.70 \text{ mdyn}/\text{Å})^{.29}$ The success of these comparisons serves to inspire confidence in the model.

Molecular Geometry of MR₄ Conformers. According to our calculations (Tables I–IV), every member of the MR₄ family exists in at least two conformationally isomeric forms: a ground state with T symmetry, and a higher energy form with S_4 symmetry. The relationship between these two symmetries is most easily appreciated by inspection of the partial subgroup lattice for neopentane shown in Figure 1. Desymmetrization of a T_d structure by a Herzberg twist leads to T symmetry, whereas symmetric deformation of two bond angles θ (Figure 1) relative to their common bisector (any one of three C_2 axes)

yields a D_{2d} structure; similar bond angle deformation of the T structure leads to D_2 symmetry. Further desymmetrization of the D_{2d} structure by a Herzberg twist also leads to D_2 symmetry, while pairwise twisting of methyl groups in opposite directions leads to an S_4 structure.

In a MR₄ structure with T symmetry, all six C–M–C or Si–M–Si bond angles are the same, i.e., tetrahedral. In a structure with S_4 symmetry, on the other hand, there are two sets of symmetry equivalent but nontetrahedral angles, one set of two, i.e., $\theta(+/M/+)$ and $\theta(-/M/-)$ as shown in Figure 1, and one set of four, i.e., $\theta(+/M/-)$. It is important to recognize that desymmetrization of a T_d structure by a pairwise twist in opposite directions necessarily (i.e., by symmetry) leads to the nonequivalence of the two sets of bond angles, i.e., necessarily leads to an S_4 structure, whereas desymmetrization by a Herzberg twist may (and, in the case of the members of the MR₄ family, does) stop at the T stage, since there is no symmetry requirement for the deformation of tetrahedral bond angles implicit in a D_2 structure.

The ligands (R) in the MR₄ family are $C(CH_3)_3$ and $Si(CH_3)_3$ groups, and the torsional behavior of the individual methyl groups therefore presents an additional complication. In molecules with T symmetry, the M–R bond lies along a C_3 axis, and the three methyls in each R group are therefore symmetry equivalent; it follows that all 12 methyl groups are symmetry equivalent. On the other hand, in molecules with S_4 symmetry the M–R bond does not lie along the symmetry axis. The three methyls in each R group are therefore symmetry nonequivalent, and it follows that the 12 methyl groups fall into three symmetry nonequivalent sets of four each.

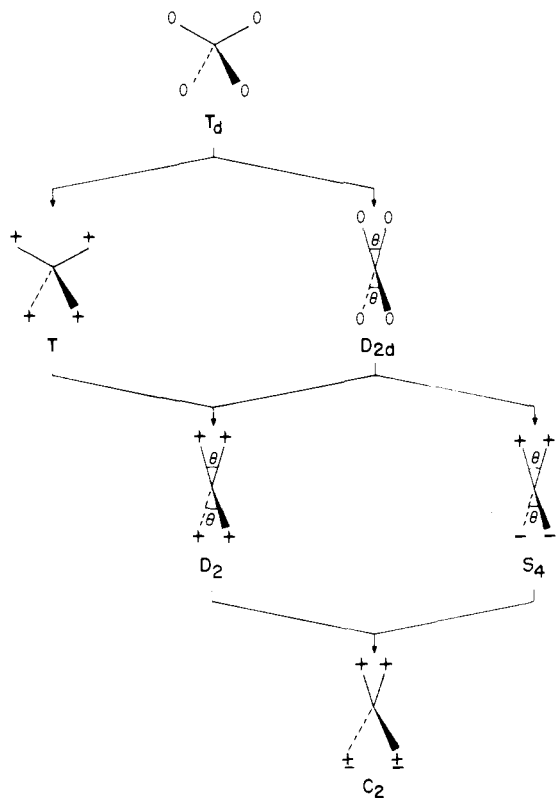**Molecules with T Symmetry.** A comparison of the ground

Figure 1. Partial subgroup lattice for neopentane. The symbols represent the sense of twist of the methyl groups relative to the completely staggered or eclipsed T_d conformation (0 = no twist; (+) or (−) = a twist of the methyl groups in a clockwise or counterclockwise direction by a fixed, arbitrary amount, $0 < \Delta\phi < \pi/3$). Only one enantiomer is shown for the T, D_2, and C_2 structures. Pairwise symmetry related angles (θ) are shown for the D_{2d}, D_2, and S_4 structures.

Table IV. Geometric Parameters Calculated for Structures of Type $M[C(CH_3)_3]_4{}^a$

	T		S_4		$\Delta E_T(S_4-$
$r°$	r	$\Delta\phi$	r	$\Delta\phi$	$T)$
1.512^b	1.628	14.7	1.634	14.6, 14.0	15.99
				−15.3, −11.1	
1.600	1.700	14.7	1.708	14.6, 13.3	14.95
				−13.8, −13.2	
1.750	1.826	14.7	1.834	13.3, 13.2	12.93
				−14.5, −13.6	
1.872^c	1.951	14.6	1.960	13.2, 13.1	11.29
				−14.3, −14.1	
1.950^d	2.029	14.6	2.038	14.2, 12.6	9.94
				−14.5, −13.4	
2.000	2.043	14.6	2.051	12.4, 12.0	9.42
				−15.0, −15.0	
2.050	2.086	14.6	2.094	12.8, 12.2	8.69
				−14.8, −14.5	
2.143^d	2.215	14.6	2.225	13.3, 11.8	6.06
				−14.0, −12.2	
2.300^e	2.312	14.3	2.319	12.9, 12.4	5.33
				−13.8, −13.3	

^{a} Parameters are defined as follows: $r°$ = preferred M–C bond length (see text), r = calculated M–C bond length. Units for $r°$ and r are Å. For definition and units of $\Delta\phi$ and ΔE_T, see Table I, footnotes d and e, replacing Si with C. ^{b} Value of $r°$ for carbon from ref 27. ^{c} Parameters for silicon from ref 28. ^{d} Parameters for germanium ($r°$ = 1.95 Å) and tin ($r°$ = 2.143 Å) are from ref 29. ^{e} The value of $r°$ for lead is taken as 2.30 Å. See "Interatomic Distances", *Chem. Soc., Spec. Publ.*, No. 11, M176 (1958).

states of molecules in the MR_4 family reveals significant trends. Consider first the series in Table IV, ranging from the severely strained **2** to the unstrained, simulated $Pb[C(CH_3)_3]_4$. The values of $\Delta\phi$ remain remarkably constant, at 14–15°, suggesting a lack of dependence on the C–M–C–C torsional constant (which varies from 0.5 kcal/mol for carbon[27] to 0.22 kcal/mol for tin[29]). This conclusion was confirmed with additional calculations on $Si[C(CH_3)_3]_4$. When the torsional constant (V_0) was "turned off", i.e., set equal to 0.0 kcal/mol, the degree of twist was still 14.8°. With V_0 = 5.0, the value of $\Delta\phi$ decreased only slightly, to 13.6°. The R groups seem to be twisted to maximize the nesting of the methyl groups induced by nonbonded interactions; indeed, when the nonbonded potentials are turned off, the molecule relaxes to a completely staggered conformation, in analogy to $Si[Si(CH_3)_3]_4$.[20]

In contrast, the distortions of valence angles, especially of the C_m–C–C_m angles, depend markedly on central bond length. The almost linear proportionality between $\theta(C_m$–C–$C_m)$ and $r°$ (Figure 2) over the range of values under examination is indicative of the relief in front strain and the concomitant decompression of C_m–C–C_m angles which accompanies an increase in $r°$. A similar trend is also observed for $\theta(C_m$–Si–$C_m)$ in the two compounds of type $M[Si(CH_3)_3]_4$ (Table I).

Since **2** is the most strained member of the series, it suffers the greatest distortion of bond lengths and angles. As a result of front strain, i.e., of overcrowding at the center of the molecule (the shortest H···H distance is 2.19 Å), the C_c–C bonds are stretched to 1.63 Å, the C_m–C–C_c bond angles are widened to 118°, and the C_m–C–C_m bond angles are compressed to 99°.[46] These distortions are in the same direction as those previously observed[47] for the closely related but less congested $HC[C(CH_3)_3]_3$, but are greater in magnitude. However, the

central bond stretching, while significant, is not exceptional for a highly strained molecule.[34] In an earlier study, Wiebenga and Bouwhuis[48] had calculated a partial structure for **2** by use of a force field based on a simplified repulsion model, and had found values of 1.74 Å and 119.6° for $r(C_c$–C) and $\theta(C_m$–C–$C_c)$, respectively. To the limited degree that comparison is possible with our results (Table II), it would appear that the previous workers overestimated the extent of distortion.

The 12 methyl groups in the T conformers are twisted in the same sense (i.e., direction) as the four $C(C_m)_3$ or $Si(C_m)_3$ groups. The greater the congestion, the less the extent of twisting: for example, in the $M[C(CH_3)_3]_4$ series, methyl twists of 4.8, 8.0, and 9.9° are calculated for M = C, Si, and Pb, respectively, and in the $M[Si(CH_3)_3]_4$ series, 3.9 and 4.6° for M = C and Si, respectively.

Molecules with S_4 Symmetry. The higher energy conformers closely resemble the ground states in two respects. First, $\Delta\phi$ values remain virtually constant, at 12–15°, regardless of internal strain (Tables I and IV). Second, internal distortions, as gauged by trends in C_m–C–C_m angle compressions, parallel those discussed for the ground states, i.e., internal strain decreases with an increase in $r°$.

However, whereas all central bond angles in the ground state are the same, those in a S_4 structure are partitioned, as we saw, into two sets. In every case, the angles in the set of two are more compressed than those in the set of four, and this differential increases with decreasing $r°$. For **2** the values are far apart (104.5 and 112.0°),[46] but as crowding decreases they tend toward the tetrahedral, e.g., for **1** they are 107.6 and 110.5°. These results are readily understood in terms of the nesting possible between R groups which are twisted in the same sense, and which subtend the central bond angles belonging to the set of two; groups twisted in the opposite sense experience greater mutual repulsion, and the central angles they subtend are thus larger.

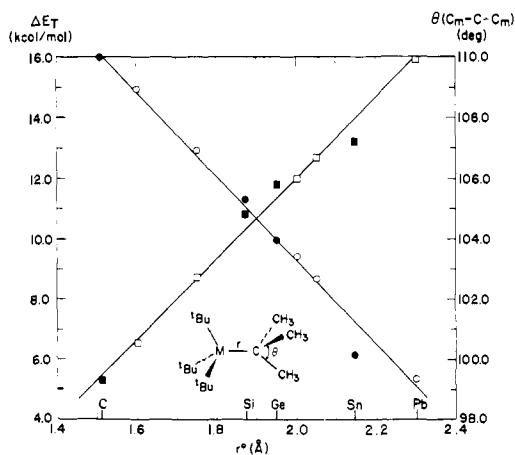The Allinger 1971 and Schleyer force fields yield compa-

Figure 2. Plots of $\theta(C_m\text{-}C\text{-}C_m)$ (squares) and ΔE_T (circles) as a function of r° for the series $M[C(CH_3)_3]_4$. Open symbols refer to simulated structures and solid symbols to nonsimulated ones (see text).

rable results for the structure of the S_4 conformer of **2** (Table II),[44,49] although the ΔE_T values differ by 2 kcal/mol. However, the torsional potentials around the S_4 structures of MR_4 molecules are very broad and shallow, and there are usually a number of structures approximately equal in energy but with widely differing $\Delta\phi$'s. In the Allinger EFF, the S_4 structure of **2** proves to be exceptionally unstable, and a slight torsional displacement flips it into a new form, lower in energy by 1.7 kcal/mol but still 14.3 kcal/mol above the ground state. The new form has C_2 symmetry, with angles of twist pairwise 3.9 and $-23°$ (Table II). The most striking effect is the behavior of $\theta(C\text{-}C_c\text{-}C)$. The calculated angles fall into two sets, {116.5, 116.5°} and {105.4, 105.7, 106.2, 107.0°}, as if the molecular symmetry were S_4, but with the relative magnitudes dramatically reversed in that the angles in the set of four are now much more compressed than those in the set of two. On the basis of our present work, we cannot exclude the possibility that C_2 conformers also exist for higher homologues of **2**.

The 12 methyl groups in S_4 conformers are generally twisted in the same sense as the $C(C_m)_3$ or $Si(C_m)_3$ groups. For example, in **1** the three sets of methyl groups are twisted by ±21.3, ±11.7, and $\pm4.9°$, in $C[Si(CH_3)_3]_4$ by ±34.8, ±5.9, and $\mp0.9°$, in $Si[C(CH_3)_3]_4$ by ±26.5, ±9.9, and $\pm2.8°$, and in simulated $Pb[C(CH_3)_3]_4$ by ±20.8, ±14.1, and $\pm9.0°$. In the C_2 conformer of **2**, three symmetry nonequivalent sets of two methyl groups each are twisted by $+47.5$, $+5.7$, $+2.0°$ (corresponding to $\Delta\phi$ 3.9°), and three others by -18.2, -2.7, and $0.0°$ (corresponding to $\Delta\phi$ $-23°$).

Both S_4 and T conformers respond to a decrease in r°, i.e., an increase in internal strain, by intramolecular avoidance maneuvers (i.e., distortions), but the response is greater for the former than for the latter. This is evident upon inspection of the ΔE_T values in Table IV, which show a marked dependence on r°. The trend is strikingly revealed in a plot (Figure 2) which shows that ΔE_T in the series $M[C(CH_3)_3]_4$ is inversely proportional to r° over the range of values examined. Furthermore, although the difference in ΔE_T values for $C[Si(CH_3)_3]_4$ and $Si[C(CH_3)_3]_4$, 9.6 and 11.3 kcal/mol, respectively, shows an effect due to the difference in $C\text{-}C_m$ and $Si\text{-}C_m$ bond lengths, comparison of ΔE_T values for the first two members ($M = C$ and Si) in each of the two series $M[C(CH_3)_3]_4$ and $M[Si(CH_3)_3]_4$ ($\Delta\Delta E_T = 4.7$ and 5.6 kcal/mol for the former and latter, respectively) suggests that the effect of changes in M on ΔE_T may be quite similar in the two series.

If the S_4 form is an intermediate in the enantiomerization of the T conformers, ΔE_T becomes a lower limit of E_{rac}, the activation energy of racemization, and the trends in ΔE_T, discussed above, will indicate trends in the lower limit of E_{rac}.

A parallel can be found in the work of Durig et al.,[18b] who found that torsional barriers around the M–C bonds in the series $M(CH_3)_4$ (M = C, Si, Ge, Sn) decrease with increasing atomic number of the central atom. Studies now underway are designed to elucidate the enantiomerization pathway and to cast further light on the dynamic stereochemistry of MR_4 molecules.

References and Notes

(1) M. Farina and C. Morandi, *Tetrahedron*, **30**, 1819 (1974).
(2) The following comments from the textbook literature typify current perceptions: (a) T symmetry. "This group is . . . very rarely, if ever, encountered in real molecules";[3a] "No definite examples of molecules belonging to this point group are known";[3b] molecules belonging to T are "Not known".[3c] (b) O symmetry. ". . . like T, [this group] is rarely if ever encountered in Nature";[3a] "No examples of molecules belonging to this point group are known";[3b] molecules belonging to O are "Not known".[3c] (c) I symmetry. "[This group] is mentioned purely for the sake of completeness, since no example of its occurrence in Nature is known".[3a]
(3) (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Wiley-Interscience, New York, N.Y., 1972, ch 3. H. H. Jaffé and M. Orchin, "Symmetry in Molecules", Chapman and Hall, London, 1972, pp 35–36; (c) J. D. Donaldson and S. D. Ross, "Symmetry and Stereochemistry", Wiley, New York, N.Y., 1972, p 37, Table 3.6.
(4) T_d symmetry is encountered in abundant variety among tetraatomic (e.g., P_4) and pentaatomic (e.g., CH_4, OsO_4, ClO_4^-, SO_4^{2-}) molecules. In general, T_d symmetry obtains for molecules of type MX_4 only if the ligands have local C_{3v} symmetry, normally $C_{\infty v}$ (X = single atom, CN, CO, N_2, C≡CH, etc.) or C_{3v} (X = CH_3, etc.). Adamantane is another example of a well-known molecule with T_d symmetry. T_h symmetry is less well represented but by no means unknown, e.g., $Ce(NO_3)_6^{3-}$ (E. L. Muetterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 109 (1967), especially p 174) and $W(N(CH_3)_2)_6$ (D. C. Bradley, M. H. Chisholm, C. E. Heath, and M. B. Hursthouse, *Chem. Commun.*, 1261 (1969)).
(5) O_h symmetry is well established in inorganic chemistry (SF_6, $Fe(CN)_6^{3-}$, $Cr(CO)_6$, etc.). The only representative in organic chemistry seems to be cubane (P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.*, **86**, 962, 3157 (1964); E. B. Fleischer, *ibid.*, **86**, 3889 (1964); J. C. Barborak, L. Watts, and R. Pettit, *ibid.*, **88**, 1328 (1966)).
(6) The classic example of I_h symmetry is $B_{12}H_{12}^{2-}$ (e.g., R. L. Middaugh in E. L. Muetterties, "Boron Hydride Chemistry", Academic Press, New York, N.Y., 1975, Chapter 8). Yet to be realized is the icosahedral "Platonic" hydrocarbon dodecahedrane (J. M. Schulman, T. Venanzi, and R. L. Disch, *J. Am. Chem. Soc.*, **97**, 5335 (1975), and references cited therein).
(7) This is a special application of a principle first enunciated by Pierre Curie, *J. Phys. (Paris)* **3**, 393 (1894); cf. also ref 1.
(8) R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem. Int. Ed. Engl.*, **5**, 385 (1966), especially p 398.
(9) An "intricate" osmium complex with O symmetry is described by D. J. Caldwell and H. Eyring, "The Theory of Optical Activity", Wiley-Interscience, New York, N.Y., 1971, pp 156–157, and decorates the cover of their book.
(10) T symmetry is beautifully illustrated by M. C. Escher's sculpture "Sphere with Fish", a beechwood sphere completely covered with relief carvings of 12 identical fish (plate 217 in B. Ernst, "The Magic Mirror of M. C. Escher", Ballantine Books, New York, N.Y., 1976).
(11) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1945, p 9.
(12) By straightforward extension, conformations with O and I symmetry may be constructed by desymmetrization of octamethylcubane and eicosamethyldodecahedrane, respectively.
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(14) H. C. Longuet-Higgins, *Mol. Phys.*, **6**, 445 (1963).
(15) C. M. Woodman, *Mol. Phys.*, **19**, 753 (1970). A wreath product formalism applicable to molecules (such as neopentane) belonging to one of the regular polytopal point groups has been devised by G. Pólya, *Acta Math.*, **68**, 145 (1937); cf. p 178, footnote 2.
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(17) If R^* is a chiral group with threefold torsional periodicity, the highest *static* symmetry of CR^*_4 is T and the molecular symmetry group[15] of the time-averaged molecule is $(C_3)^4 \wedge T$, of order 972.
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(19) L. S. Bartell, F. B. Clippard, Jr., and T. L. Boates, *Inorg. Chem.*, **9**, 2436 (1970).
(20) J. P. Hummel, J. Stackhouse, and K. Mislow, *Tetrahedron*, **33**, 1925 (1977).
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(30) An additional torsional constant (V_0) of 0.5 kcal/mol was used for M–C–C–H dihedral angles.

(31) Good agreement has been found between the calculated[29] and microwave[32] structures of CH₃CH₂GeH₃.

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(36) The input structures for M[X(CH₃)₃]₄, M = C, Si, Ge, Sn, and X = C, Si, had T_d symmetry, with standard bond lengths and bond angles and all bonds staggered (60°). For the simulation, the input structure for a given molecule was the minimized structure with the next smallest value of r^0 (cf. Table IV). All the above input structures relaxed to T symmetry. The S_4 structures were obtained by putting in the appropriate minimized T structure, with two of the groups rotated from $+\Delta\phi$ to $-\Delta\phi$.

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(39) An instructive example is provided by hexamethylethane. Using the <0.01 (kcal/mol)/iteration criterion, the total steric energy[35] E_T is 13.37 kcal/mol

using the Schleyer force field,[40] and 4.93 kcal/mol using Allinger's,[27] with central C–C bond distances of 1.574 and 1.564 Å, respectively. Using the process of optimization "from both sides", we find E_T = 12.51 (1.571 Å) and 3.06 kcal/mol (1.557 Å), respectively. The same result is obtained by using a smaller energy criterion for minimization, e.g., <0.0001 (kcal/mol)/iteration (E_T = 12.41 and 3.08, respectively,[41] and E_T = 12.49 and 3.07 kcal/mol, respectively[42]). However, it seems to have escaped attention that the global minima thus calculated correspond to conformations with D_3 symmetry (ϕ = 44.3 and 41.4°, respectively), whereas the structures with higher E_T's (obtained without the above precautions) correspond to transition state conformations located on very shallow plateaus, whose symmetry is D_{3d} (S. Baxter, unpublished results).

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(44) We also tried out an EFF developed by Allinger in 1973.[45] After sufficient bond stretching has occurred, the cubic term of the stretching function in this force field becomes increasingly important and imparts a marked anharmonicity to the stretching potential. As a result, the C$_c$–C bond lengths calculated for the highly strained hydrocarbon **2** by use of this force field continue to increase without limit, and an optimized structure cannot be attained; in effect, the bonds are homolyzed.

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(46) These values are obtained by use of the Allinger (1971) force field. Other force fields give similar results (Table II).

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(49) In the MUB-2 force field,[43] input structures with S_4 symmetry minimized to the T conformer.

Reactions of Potassium–Graphite

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Abstract: Potassium–graphite, a typical alkali metal–graphite intercalation compound, has been found to undergo reactions with organic substrates by both one- and two-electron processes. The reaction of weak protic acids like water and alcohols with C₈K proceeds both by simple deprotonation of the protic acid by the Lewis base C₈K to give a partially reduced graphite and by reduction leading to hydrogen formation. ESCA spectra of the graphite product of these reactions, titrations of soluble base in these reactions of C₈K and proton sources, and measurement of the amount of hydrogen evolved on reaction of C₈K and an alcohol all suggest that the reactivity of C₈K toward proton acids is substrate size dependent. In general, Lewis base abstraction of a proton by C₈K seems to be more important with smaller alcohols. One-electron processes may be relatively more important in reactions of larger alcohols at the surface or edges of C₈K. The acid–base chemistry of rubidium–graphite and cesium–graphite was shown to be similar to that observed for C₈K. Study of products formed on reaction of alkyl halides with C₈K show that one-electron transfer is an important reaction pathway for reductions with potassium–graphite. Characteristic radical rearrangements observed in the reduction of 5-hexenyl halides provided positive evidence for the intermediacy of free radicals. Attempts to trap carbanionic intermediates or alkylpotassium species with magnesium bromide were unsuccessful. However, transient carbanionic species or alkyl halide radical anions may have been present since reduction of tetrahydrofurfural chloride with C₈K led to the rearranged product, penten-5-ol. Typical products observed in reductions of alkyl chlorides were alkanes. Alkyl iodides reacted with C₈K to give Wurtz coupled products. Alkyl bromides had reactivity patterns intermediate between that of alkyl chlorides and alkyl iodides. Other substrates were also briefly examined and the reductions observed in these cases generally correlated well with known chemistry of soluble aromatic radical anions like sodium naphthalene. The usefulness of potassium–graphite as a polymeric reagent was evaluated.

Graphite readily forms intercalation compounds with both electron donor and electron acceptor molecules in which intercalated molecules are inserted between the planes of the original graphite structure.[1] These intercalation compounds have been used as catalysts[2] and as reagents[3] in a number of reactions and, in addition, possess somewhat unusual physical characteristics such as modified electronic properties[4] and a distinctive solid state structure.[5] Our interest in this class of compounds arose primarily as a result of the unusual chemical and physical properties of alkali metal–graphites such as potassium–graphite. We were specifically intrigued by the catalytic activity of potassium–graphite[6] and the surprising

similarity of potassium–graphite to group 8 metals in reactions like catalytic hydrogenation and Fischer–Tropsch synthesis.[7] Alkali metal–graphites such as potassium–graphite are presumably related to the polycyclic aromatic radical anions generated in the reduction of coal or heavy oils by strong reducing agents.[8] The reduced species formed in these reactions are presently of interest as intermediates for the derivatization of coal or petroleum tars. Alkali metal–graphites would also be heterogeneous analogues of the well-studied homogeneous aromatic radical anions[9] and might be expected to act as polymeric versions of these reagents.[10] Since the reducing ability of alkali metal–graphites is an essential aspect of their