5492 *J. Phys. Chem. A* **2003,** *107,* 5492−5498

Structural and Energetics Studies of Tri- and Tetra-*tert*-butylmethane

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Received: April 3, 2003

Applying the G3 and G3(MP2) models and using both the isodesmic and atomization schemes, the heats of formation (ΔH_f) at 0 and 298 K are calculated for mono-*tert*-butylmethane (2,2-dimethylpropane or neopentane, abbreviated as mono-TBM), di-*tert*-butylmethane (di-TBM), tri-*tert*-butylmethane (tri-TBM), and tetra-*tert*-butylmethane (tetra-TBM). Upon examining the results, it is found that all of the calculated ΔH_{f298} values are well within ±10 kJ mol^{-1} of the available experimental data for the first three compounds. Hence, for tetra-TBM, a compound that has not yet been synthesized, the G3(MP2) results reported in this work should be reliable estimates. Moreover, we have found that the atomization scheme is slightly more suitable for the study of the smaller molecules, while the isodesmic scheme is more suitable for the larger molecules. Structurally, it is found that the equilibrium structures of mono-TBM, di-TBM, tri-TBM, and tetra-TBM have T_d, C_2, C_1, and T symmetry, respectively. The energy-minimized structure of each TBM molecule is determined and all structural parameters are generally in good agreement with the available experimental data. Furthermore, it is found that the innermost C−C bond lengths increase along the series mono-TBM < di-TBM < tri-TBM < tetra-TBM, a trend that is expected from steric consideration.

1. Introduction

Tri-*tert*-butylmethane (tri-TBM), a saturated hydrocarbon molecule, is noteworthy because of the great intramolecular congestion arising from packing three bulky *tert*-butyl groups around a tertiary carbon atom. It is a classic molecule of unusual properties, which has intrigued and challenged chemists for over 30 years. Tri-TBM was first synthesized by Stiles and Lee in 1971.[1] Later, Bartell and Burgi conducted an electron diffraction study.[2,3] They attempted to determine the structure of this highly strained molecule to illuminate its properties and explain its unusual vibrational spectra. However, due to the limited resolution of the electron diffraction data, severe approximations had to be made in the process of its structural determination. Thus, it not only was assumed that the molecule had overall C_3 symmetry, but it was also supposed that the individual *tert*-butyl groups were constrained to (local) C_{3v} symmetry. This problem was pointed out by Bartell and Burgi in their initial paper[2] where they noted: "...this adds to the evidence that the model with local C_{3v} symmetry is too restrictive and that more, though probably quite limited, information can be extracted from the experimental data." In 1994, Hagler et al. reinterpreted the experimental structure of tri-TBM by Hartree−Fock, density functional theory, and class II force field methods.[4] Afterward, in 1998, Palmo et al. also studied the structure and the vibrational frequencies of tri-TBM by a spectroscopically determined force field (SDFF).[5] However, energetics and structural studies of tri-TBM with high-level molecular orbital theory are still unavailable.

Tetra-*tert*-butylmethane (tetra-TBM), which has not been synthesized yet, is even more crowded around the central carbon atom than tri-TBM. We are interested in the structure of this molecule and are intrigued by its very long C−C bonds. We intend to compare the bond lengths of these long bonds with those found in other highly congested saturated hydrocarbon molecules.

Mono- and di-*tert*-butylmethane (denoted as mono-TBM and di-TBM, respectively) are lower homologues of tri-TBM and tetra-TBM. It is clear that di-TBM is significantly less strained than tri-TBM. Meanwhile, mono-TBM is generally considered to be unstrained. It has been the subject of several previous electron diffraction studies.[6,7,20]

In our previous studies on $(CH)_6$ isomers,[8,9] the heats of formation at 0 K (ΔH_{f0}) and at 298 K (ΔH_{f298}) were calculated with the Gaussian-2 (G2)[10] and Gaussian-3 (G3)[11] based methods. In our first study on $(CH)_6$ isomers,[8] it was found that the G2 methods suffer "an unfavorable accumulation of component small errors".[12] Furthermore, this shortcoming may be circumvented by using isodesmic reactions in the computation scheme.[12,13] On the other hand, in our subsequent study on the $(CH)_6$ isomers,[9] it was found that the aforementioned error accumulation is significantly reduced in the G3 methods and hence the ΔH_f values of molecules with the size of benzene may be calculated directly, i.e., using the atomization scheme. This result is important, as, for some compounds, isodesmic reactions cannot always be written readily. More recently, the 12 monocyclic azines with the general formula $N_n(CH)_{6-n}$, n = 1, 2, ..., 6,[14] and 19 boranes with 1 to 10 boron atoms[15] have been studied in a similar fashion by using the G3[11] and G3(MP2)[16] models of theory. Upon examining the results, it is found that the geometrical parameters optimized at the MP2(Full)/6-31G(d) level are in general in very good agreement with experiment. Also, most of the calculated ΔH_{f298} values are well within ±10 kJ mol^{-1} of the experimental data. Hence, it may be once again concluded that the unfavorable accumulation of component errors found in the G2-based methods has been markedly reduced in the G3 methods.

In the present work, the structures of the aforementioned TBM molecules are determined and their ΔH_{f0} and ΔH_{f298} values are

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10.1021/jp034879r CCC: $25.00

calculated by using the G3 and G3(MP2) methods. Both the atomization[8,9,12,17] and isodesmic[12,13] schemes are used in the calculation of ΔH_f values. The purpose of the present study is two-fold. First, energetically, by comparing the calculated results of G3 and G3(MP2) atomization and the isodesmic schemes with the available experimental values, the more suitable scheme in the study of the TBM molecules can be found. Additionally, if the calculation method proves to be trustworthy, the calculated ΔH_f results for tetra-TBM, an unknown compound so far, should be reliable estimates. Second, structurally, congestion around the central carbon atom increases in the series mono-TBM < di-TBM < tri-TBM < tetra-TBM. We intend to study the effect of this congestion on the structure and symmetry of tri-TBM and tetra-TBM.

2. Methods of Calculation and Results

All calculations were carried out on various workstations with the Gaussian 98 package of programs.[18] The methods of calculation employed, G3 and G3(MP2), are briefly described below.

In the G3 method, geometry optimization is carried out at the MP2(Full)/6-31G(d) level. To determine the energy E_e of a structure, single-point calculations at the levels of QCISD(T)/6-31G(d), MP4/6-31G(d), MP4/6-31+G(d), MP4/6-31G(2df,p) and MP2(Full)/G3large, all based on the optimized structure, are carried out. In addition, a higher level correction (HLC) is applied in the calculation of E_e. The HF/6-31G(d) vibrational frequencies, scaled by 0.8929, are applied for the zero-point vibrational energy (ZPVE) correction at 0 K ($E_0 = E_e + \mathrm{ZPVE}$). In the G3(MP2) model, again based on the geometry optimized at the MP2(Full)/6-31G(d) level, frozen-core single-point calculations QCISD(T)/6-31G(d) and MP2/G3MP2large are carried out. Also, HLC and ZPVE corrections are applied. The error bar for these methods for systems with the size of the aforementioned TBM molecules is expected to be less than or about ± 10 kJ mol^{-1}.

After calculating the total energies at 0 K (E_0) and the enthalpies at 298 K (H_{298}), the results were then converted into ΔH_f values for the TBM molecules by using the atomization scheme[8,9,12,17] and the isodesmic scheme.[12,13] In the atomization scheme, the experimental[19] ΔH_{f0} values of C (711.2 kJ mol^{-1}) and H (216.0 kJ mol^{-1}), as well as the experimental[19] ΔH_{f298} values of C (716.7 kJ mol^{-1}) and H (218.0 kJ mol^{-1}), are required. We used equations similar to those given in the paper by Radom et al.[17] for the calculation of the ΔH_{f298} value of a given TBM:

$$\Delta H_{f298}[\mathrm{TBM}] = H_{298}[\mathrm{TBM}] - x\{H_0[\mathrm{C_{(g)}}] + 0.00236\} - y\{H_0[\mathrm{H_{(g)}}] + 0.00236\} + x\Delta H_{f298}{}^{\mathrm{exp}}[\mathrm{C_{(g)}}] + y\Delta H_{f298}{}^{\mathrm{exp}}[\mathrm{H_{(g)}}] \quad (1)$$

$$\Delta H_{f298}[\mathrm{TBM}] = H_{298}[\mathrm{TBM}] - x\{H_0[\mathrm{C_{(g)}}] + 0.00249\} - y\{H_0[\mathrm{H_{(g)}}] + 0.00236\} + x\Delta H_{f298}{}^{\mathrm{exp}}[\mathrm{C_{(g)}}] + y\Delta H_{f298}{}^{\mathrm{exp}}[\mathrm{H_{(g)}}] \quad (2)$$

$$\Delta H_{f298}[\mathrm{TBM}] = \Delta H_{f0}[\mathrm{TBM}] + \Delta H_{298}{}^{\mathrm{calc}}[\mathrm{TBM}] - x\Delta H_{298}{}^{\mathrm{exp}}[\mathrm{C_{(s)}}] - (y/2)\Delta H_{298}{}^{\mathrm{exp}}[\mathrm{H_{2(g)}}] \quad (3)$$

where x and y are the number of C and H atoms, respectively, in the TBM molecule. We note that eq 1 is more commonly used in the calculation of ΔH_{f298} values. In eq 2, we have replaced the calculated ΔH_{298} (which is $H_{298} - H_0$, and H_0 is simply E_0) value of $\mathrm{C_{(g)}}$ (6.196 kJ mol^{-1}, or 0.00236 hartree) with the experimental result (6.535 kJ mol^{-1}, or 0.00249 hartree). Such a replacement was first proposed by Radom et al.[17] One other way to obtain ΔH_{f298} values is to apply eq 3, which has also been suggested by Radom et al.[17]

TABLE 1: The Electronic Energy (E_e) (in hartrees) for Mono-TBM, Di-TBM, Tri-TBM, and Tetra-TBM

			E_e at HF/6-31G(d)[a]	E_e at MP2(Full)/6-31G(d)[a]
mono-TBM	C_5H_{12}	T_d	−196.33382 (0)	−197.02325 (0)
di-TBM	C_9H_{20}	C_2	−352.45511 (0)	−353.70094 (0)
di-TBM	C_9H_{20}	C_{2v}	−352.45440 (1)	−353.70006 (1)
tri-TBM	$C_{13}H_{28}$	C_1	−508.52125 (0)[b]	−510.33783 (0)
tri-TBM	$C_{13}H_{28}$	C_3	−508.52125 (0)	−510.31558 (3)
tetra-TBM	$C_{17}H_{36}$	T	−664.54128 (0)	−666.94137 (0)
tetra-TBM	$C_{17}H_{36}$	T_d	−664.46634 (10)	−666.86325 (13)

[a] The number of imaginary frequencies calculated for each molecule is given in parentheses. [b] The optimized geometry has C_3 symmetry, even though no symmetry constraint was imposed initially.

In the isodesmic scheme,[12,13] we combined the bond separation reactions of Raghavachari et al.[13] with the G3 and G3(MP2) models of theory. Specifically, the isodesmic bond separation reactions for our TBM molecules are

$$\mathrm{CH_3}(\textit{tert}\text{-butyl}) + 3\mathrm{CH_4} \rightarrow 4\mathrm{C_2H_6} \quad (4)$$

$$\mathrm{CH_2}(\textit{tert}\text{-butyl})_2 + 7\mathrm{CH_4} \rightarrow 8\mathrm{C_2H_6} \quad (5)$$

$$\mathrm{CH}(\textit{tert}\text{-butyl})_3 + 11\mathrm{CH_4} \rightarrow 12\mathrm{C_2H_6} \quad (6)$$

$$\mathrm{C}(\textit{tert}\text{-butyl})_4 + 15\mathrm{CH_4} \rightarrow 16\mathrm{C_2H_6} \quad (7)$$

To obtain the G3 ΔH_f of the TBM molecules by using the isodesmic scheme, we require the experimental[19] ΔH_{f0} values (in kJ mol^{-1}) of $\mathrm{CH_4}$ (−66.8) and $\mathrm{C_2H_6}$ (−68.4) and the ΔH_{f298} values (in kJ mol^{-1}) of $\mathrm{CH_4}$ (−74.5) and $\mathrm{C_2H_6}$ (−84.0). Moreover, we also require the E_0 and H_{298} values of $\mathrm{CH_4}$ and $\mathrm{C_2H_6}$ calculated at the G3 and G3(MP2) levels, and these values are included in the footnotes of Tables 2 and 3.

Table 1 lists the electronic energy (E_e) of the TBM molecules calculated with different symmetry constraints. In Table 2, the G3 and G3(MP2) E_0 and the ΔH_{f0} values of the TBM molecules are shown. The G3 and G3(MP2) H_{298} and the ΔH_{f298} values for the molecules are summarized in Table 3, along with available experimental data for ready comparison.

The structural parameters of the TBM molecules, optimized at the MP2(Full)/6-31G(d) level, are tabulated in Table 4. Also included in this table are the available experimental structural data as well as those calculated at other theoretical levels. The molecular structures and the labeling of the atoms for the TBM molecules are shown in Figure 1.

3. Discussion

In this section we discuss the calculated results of the four TBM molecules. Where possible, we compare the G3 or G3(MP2) structural and energetics results with the available experimental data.

3.1. Mono-*tert*-butylmethane (mono-TBM). Mono-TBM, also known as neopentane, is generally considered to be unstrained. From our study, we found that mono-TBM is a highly symmetrical molecule with T_d geometry. In Table 4, we see that the optimized bond lengths for $\mathrm{C_t{-}C_m}$ (1.528 Å) and $\mathrm{C_m{-}H_m}$ bonds (1.095 Å) are in good agreement with the vapor-phase electron diffraction average:[20] 1.537 ± 0.003 and 1.114

TABLE 2: The Total Energies (in hartrees) at 0 K (E_0) and the Heats of Formation (kJ mol^{-1}) at 0 K (ΔH_{f0}) for Mono-TBM, Di-TBM, Tri-TBM, and Tetra-TBM Calculated at the G3 and G3(MP2) Levels, Using the Atomization and Isodesmic Schemes

		E_0 G3	E_0 G3(MP2)	ΔH_{f0}[a] G3 (atomization)	ΔH_{f0}[b] G3 (isodesmic)	ΔH_{f0}[a] G3(MP2) (atomization)	ΔH_{f0}[b] G3(MP2) (isodesmic)
mono-TBM	T_d	−197.54392	−197.36164	−135.7	−134.2	−134.5	−133.9
di-TBM	C_2	−354.62505	−354.29595	−189.6	−187.9	−188.4	−187.3
di-TBM	C_{2v}	−354.62411	−354.29501	−187.2	−185.5	−185.9	−184.8
tri-TBM	C_1		−511.19400			−147.1	−145.5
tri-TBM	C_3		−511.17276			−91.4	−89.7
tetra-TBM	T		−668.06250			−28.3	−26.1
tetra-TBM	T_d		−667.99310			153.9	156.1

[a] To obtain these ΔH_{f0} values, we require the E_0 values of the TBM molecules and the E_0 values of the constituent atoms. At the G3 level, the E_0 values for C and H are −37.82772 and −0.50100 hartrees, respectively. At the G3(MP2) level, the corresponding values are −37.78934 and −0.50184 hartrees. [b] To obtain these ΔH_{f0} values, we require the E_0 values of CH_4 (−40.45762 hartrees) and C_2H_6 (−79.72339 hartrees) at the G3 level. At the G3(MP2) level, the corresponding values are −40.42210 and −79.65120 hartrees.

TABLE 3: The Enthalpies at 298 K (H_{298}) and the Heats of Formation (kJ mol^{-1}) at 298 K (ΔH_{f298}) for Mono-TBM, Di-TBM, Tri-TBM, and Tetra-TBM Calculated at the G3 and G3(MP2) Levels, Using the Atomization and Isodesmic Schemes

		H_{298} G3	H_{298} G3(MP2)	ΔH_{f298}[a] G3 (atomization)	ΔH_{f298}[b] G3 (isodesmic)	ΔH_{f298}[a] G3(MP2) (atomization)	ΔH_{f298}[b] G3(MP2) (isodesmic)	ΔH_{f298} (experiment)
mono-TBM	T_d	−197.53585	−197.35354	−168.3	−169.3	−167.0	−169.0	−167.9 ± 0.63[c]
				−170.0		**−168.7**		
				−170.6		*−169.3*		
di-TBM	C_2	−354.61186	−354.28276	−245.2	−248.3	−243.9	−247.6	−241.5 ± 1.5[d]
				−248.3		**−247.0**		
				−249.1		*−247.9*		
di-TBM	C_{2v}	−354.61169	−354.28259	−244.8	−247.9	−243.5	−247.2	
				−247.8		**−246.6**		
				−248.7		*−247.4*		
tri-TBM	C_1		−511.17585			−226.0	−231.4	−235.2 ± 4.3[e]
						−230.4		
						−231.6		
tri-TBM	C_3		−511.15462			−170.3	−175.7	
						−174.7		
						−176.0		
tetra-TBM	T		−668.04061			−133.7	−140.9	
						−139.5		
						−141.1		
Tetra-TBM	T_d		−667.95964			78.9	71.7	
						73.1		
						71.5		

[a] We use eqs 1, 2, and 3 of the atomization scheme to obtain the ΔH_{f298} values shown in normal font, bold font, and italic font, respectively. For the calculation of these values, we need the H_{298} values listed in the table and also the H_{f298} values for the constituent atoms. [b] To obtain these ΔH_{f298} values, we require the H_{298} values of CH_4 (−40.45381 hartrees) and C_2H_6 (−79.71891 hartrees) at the G3 level. At the G3(MP2) level, the corresponding values are −40.41828 and −79.64672 hartrees. [c] Reference 21. [d] Reference 26. [e] Reference 27.

± 0.008 Å, respectively. Moreover, the calculated $C_tC_mH_m$ angle (110.9°) is also in excellent accord with the experimental results, 112.2 ± 2.8°.[20] The C_t-C_m bond (1.528 Å) of mono-TBM is the shortest innermost C−C bond found in the TBM molecules studied in this work.

We now turn our attention to the calculated ΔH_f values. In Table 3, it is seen that the ΔH_{f298} values of mono-TBM are −168.3, −170.0, and −170.6 kJ mol^{-1}, using the three slightly different atomization schemes at the G3 level, while the corresponding ΔH_{f298} values at the G3(MP2) level are −167.0, −168.7, and −169.3 kJ mol^{-1}. These two sets of values are in excellent agreement with the experimental result,[21] −167.9 ± 0.63 kJ mol^{-1}. The corresponding ΔH_{f298} values of mono-TBM from the isodesmic scheme are −169.3 and −169.0 kJ mol^{-1}, also in excellent agreement with experiment. From these comparisons, it is seen that there is no accumulation of systematic errors[12] in the atomization scheme for this molecule, which is not unexpected for molecules of this size. In any event, both G3 and G3(MP2), coupled with either the atomization or isodesmic scheme, yield excellent results for mono-TBM.

Before proceeding further, we briefly comment on the results obtained by the three different atomization schemes, i.e., eqs 1−3. First, the results of these three methods, for all four TBM molecules, are in accord with each other to well within ±10 kJ mol^{-1}, the generally accepted error range of the G3 methods. In other words, these three methods yield results of very similar quality. Furthermore, the ΔH_{f298} values generated from eqs 2 and 3 of the atomization scheme are very close to that obtained with the isodesmic scheme.

3.2. Di-*tert*-butylmethane (di-TBM). Di-TBM is slightly more strained than mono-TBM. Both the C_2 and C_{2v} structures of di-TBM have been studied. In Table 1, we can see that the C_2 structure is an energy-minimized structure, while the C_{2v} structure is a transition structure (TS) with one imaginary vibrational frequency. Upon intrinsic reaction coordinate analysis,[22,23] it is found that the C_{2v} structure is the TS connecting two C_2 structures, which are mirror images of each other. At the MP2(Full)/6-31G(d) level, the barrier of this rearrangement is 2.3 kJ mol^{-1}. At the G3 and G3(MP2) levels, this barrier is reduced to about 0.4 kJ mol^{-1}. Clearly, this molecule is not very rigid. This finding is consistent with the conclusion of

TABLE 4: Structural Parameters (in Å and Degrees) of Mono-TBM, Di-TBM, Tri-TBM, and Tetra-TBM Optimized at the MP2(Full)/6-31G(d) Level

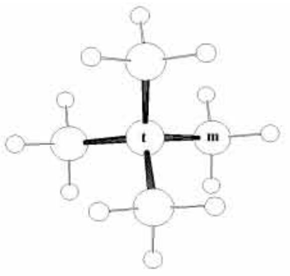
parameter	calcd	calcd	exptl	other[b]	parameter	calcd	calcd	exptl	other[b]
				mono-*tert*-butylmethane T_d					
C_t-C_m	1.528		1.537 ± 0.003[a]		$C_tC_mH_m$	110.9		112.2 ± 2.8[a]	
C_m-H_m	1.095		1.114 ± 0.008[a]		$H_mC_mH_m$	108.0			
$C_mC_tC_m$	109.5								
				di-*tert*-butylmethane					
	C_2	C_{2v}				C_2	C_{2v}		
C_t-C_q[c]	1.547	1.546	1.545 av[a]	1.552	$H_tC_tH_t$	105.3	105.4	105.0[a]	
C_q-C_m[d]	1.534	1.535	1.545 av[a]	1.537	$C_qC_tC_q$	124.6	126.0	125−128[a]	
	1.532	1.530			$C_tC_qC_m$	106.0	105.4	106.4[a]	105.6
	1.528					112.1	113.3	112.6[a]	114.9
C_t-H_t	1.100	1.101	1.122 av[a]	1.100 ave		113.8		115.2[a]	112.0
C_m-H_m	1.095	1.095	1.122 av[a]	1.100 ave	$C_qC_mH_m$	110.7	110.6		
	1.095	1.095				110.8	111.2		
	1.095	1.095				111.3			
	1.096	1.096			$C_qC_tC_qC_m$	167.6	180.0		
	1.095	1.095							
	1.093	1.091							
	1.096								
	1.096								
	1.090								
				tri-*tert*-butylmethane					
	C_1	C_3				C_1	C_3		
C_t-C_q[c]	1.600	1.622	1.611 ± 0.005[e]	1.618	$C_mC_qC_m$	108.8	105.7	105.8 av[e]	101.8
	1.600					101.7	101.6		105.9
	1.600					105.7			108.8
C_q-C_m[d]	1.537	1.535	1.548 av[e]	1.544	$C_qC_mH_m$	111.7	112.5	114.2 av[e]	108.7
	1.543	1.548		1.553		107.7	108.3		109.1
	1.548			1.565		114.3	113.6		109.6
C_t-H_t	1.102	1.105	1.111 av[e]	1.088		114.9	112.9		111.4
C_m-H_m	1.084	1.084	1.111 av[e]	1.077−1.087		109.0	108.3		112.0
	1.095	1.093				110.6			112.1
	1.096	1.089				113.3			114.0
	1.095	1.096				112.1			114.3
	1.093					108.8			115.4
	1.087				$C_qC_tH_t$	102.9	102.1	101.6[e]	102.4
	1.091				$H_mC_mH_m$	107.1	107.2		104.5
	1.089					106.5	105.6		106.6
	1.096					106.5	108.4		106.7
$C_qC_tC_q$	115.2	115.7	116.0 ± 0.4[e]	115.5		108.3	107.0		107.1
$C_tC_qC_m$	110.9	113.2	113.0 av[e]	110.6		107.3			107.2
	114.7	116.2		114.1		107.9			107.4
	114.1			114.8		107.0			108.3
						107.4			109.5
					$C_mC_qC_tH_t$	39.1	57.5		
				tetra-*tert*-butylmethane					
	T	T_d				T	T_d		
C_t-C_q[c]	1.661	1.723		1.683	$C_qC_mH_m$	107.1	106.5		107.6
C_q-C_m[d]	1.553	1.554		1.565		113.5	114.6		114.0
C_m-H_m	1.087	1.081		1.074−1.088		114.5			116.2
	1.095	1.093			$H_mC_mH_m$	106.1	105.5		105.2
	1.084					106.5	108.8		105.4
$C_qC_tC_q$	109.4	109.4				108.5			107.5
$C_tC_qC_m$	115.7	117.0		115.9	$H_mC_mC_qH_m$	116.7	116.5		
$C_mC_qC_m$	102.6	100.9		102.4		117.8			
					$C_mC_qC_tC_q$	75.9	60.0		

[a] Reference 20. [b] Data for mono- and di-TBM are experimental results taken from ref 24. Data for tri- and tetra-TBM are spectroscopically determined force field (SDFF) results taken from ref 5. [c] t = tertiary, q = quaternary. [d] m = methyl. [e] Reference 3.

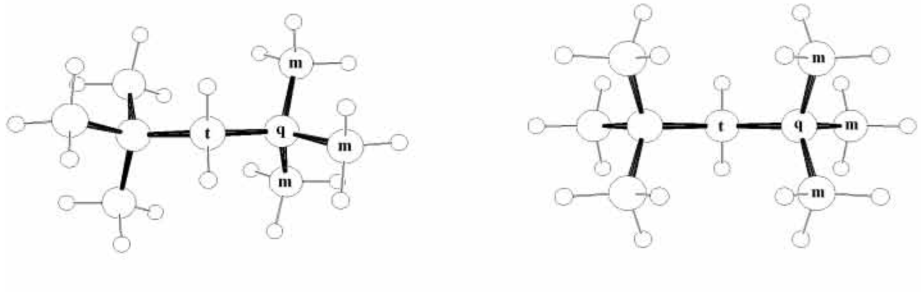
Bartell and Bradford[20] that di-TBM "exhibits striking steric deformations due to its pair of inescapable GG′ (*gauche*−*gauche*′) conformations". Examining the structure of the TS more closely, it is found that the two adjacent *tert*-butyl groups of the TS respond to the steric stress by undergoing torsional displacements of 12° to form the minimum C_2 structure.

In Table 4, we see that the optimized bond lengths for the central C_t-C_q bonds (1.547 Å) and the C_t-H_t bond (1.100 Å) are in very good agreement with the vapor-phase electron diffraction average:[20] 1.545 ± 0.005 and 1.122 ± 0.015 Å, respectively. Also, the calculated $C_qC_tC_q$ angle (124.6°) is in excellent accord with the experimental results, 125−128°.[20] Furthermore, our results are also in agreement with those obtained by MM3 and lower level ab initio methods.[24] It is also noted here that the C_t-C_q bond (1.547 Å) of di-TBM is longer than the C_t-C_m bond (1.528 Å) of mono-TBM. The lengthening of the innermost C−C bonds indicates the increase of strain from mono-TBM to di-TBM.

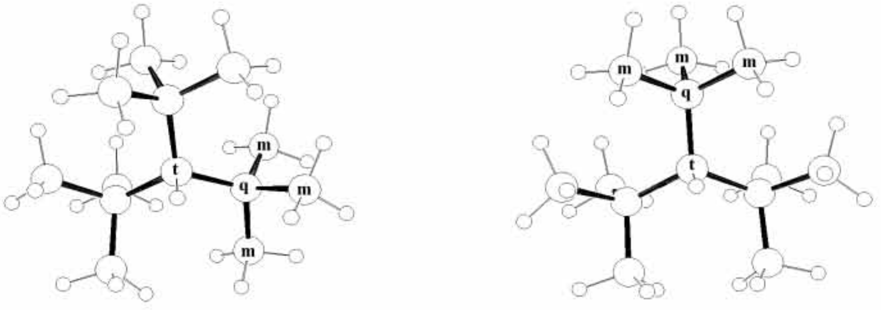
In the work of Bartell and Bradford,[20] the authors noted that the two adjacent *tert*-butyl groups of di-TBM undergo torsional displacements, tilting away from each other and opening up the central $C_qC_tC_q$ bond angle to 125−128° to release the steric



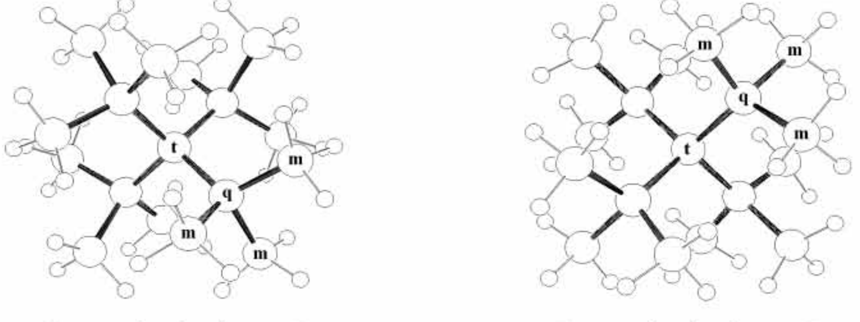
Mono-*tert*-butylmethane T_d



Di-*tert*-butylmethane C_2 Di-*tert*-butylmethane C_{2v}



Tri-*tert*-butylmethane C_1 Tri-*tert*-butylmethane C_3



Tetra-*tert*-butylmethane T Tetra-*tert*-butylmethane T_d

Figure 1. The molecular structures and labeling of atoms for mono-TBM, di-TBM, tri-TBM, and tetra-TBM.

stress of the molecule. It should be pointed out that the central $C_qC_tC_q$ bond angle in di-TBM is extremely large for a tetrahedrally coordinated central atom; the “unstrained” CCC bond angles about secondary carbons are usually found to be 113−114°. As pointed out by Mislow,[25] any departure from the tetrahedral angle disturbs the σ character of the bonds and leads to the formation of bent bonds. He also postulated that, with increasing angle bending, there is a corresponding change in hybridization.

Referring to the thermochemical data reported in Table 3, it is seen that the G3 and G3(MP2) ΔH_{f298} values of di-TBM are -245.2 and -243.9 kJ mol^{-1}, respectively, using eq 1 of the atomization scheme. These two values are in excellent agreement with the experimental result,[26] -241.5 ± 1.5 kJ mol^{-1}. The corresponding ΔH_{f298} values of di-TBM with the isodesmic scheme are -248.3 and -247.6 kJ mol^{-1}, also in very good agreement with experiment. From these comparisons, it is again seen that, as in the case of mono-TBM, there is hardly any accumulation of systematic errors[12] in the atomization scheme for this molecule. Indeed, with eq 1, for both mono-TBM and di-TBM, the atomization scheme leads to slightly better results.

For mono-TBM and di-TBM, both the G3 and G3(MP2) methods yield accurate ΔH_{f298} results. Indeed for di-TBM, the lower level G3(MP2) method yields even marginally better ΔH_{f298} values. For the larger molecules of tri-TBM and tetra-TBM, the resource requirement of G3 calculations would be prohibitively high. Hence we will only employ the G3(MP2) method for these larger systems. On the basis of our experience with mono-TBM and di-TBM, the G3(MP2) results for tri-TBM and tetra-TBM should still be reliable.

3.3. Tri-*tert*-butylmethane (tri-TBM). Tri-TBM is a highly crowded and strained molecule. In this work, both the C_3 and C_1 structures of tri-TBM have been studied. At the HF/6-31G(d) level, the C_3 structure, with all real vibrational frequencies, represents an energy minimum. However, at the MP2(Full)/6-31G(d) level, the C_3 structure has three imaginary vibrational frequencies and hence cannot be an equilibrium structure. Instead, we now have the C_1 structure representing the energy minimum. As we shall see below, employing this C_1 structure to calculate the G3(MP2) ΔH_f values for tri-TBM yields results that are in very good agreement with experiment. Hence, we may conclude that the equilibrium structure of tri-TBM has C_1 symmetry.

In Table 4, we see that the optimized bond lengths for the central C_t-C_q bonds (1.600 Å, within three decimal places) and the C_t-H_t bond (1.102 Å) of the C_1 structure are in very good agreement with the gas-phase electron diffraction average:[3] 1.611 ± 0.005 and 1.111 ± 0.003 Å, respectively. It is noted that, in this experimental study, C_3 symmetry was assumed throughout. Moreover, the calculated $C_qC_tC_q$ angle (115.2°) is also in excellent accord with the experimental result, 116.0 ± 0.4°.[3] Furthermore, our results are also in agreement with those obtained by a spectroscopically determined force field (SDFF) and lower level ab initio methods.[5] It is of interest to note here that the innermost C_t-C_q bond (1.600 Å) of the tri-TBM is significantly longer than the C_t-C_q bond (1.547 Å) of di-TBM and the C_t-C_m bond (1.528 Å) of mono-TBM. The lengthening of the innermost C−C bonds indicates the increase of strain from mono-TBM < di-TBM < tri-TBM. Also, the central C_t-C_q bond of the C_3 structure is 1.622 Å, longer than that of the C_1 structure (1.600 Å). This is due to the large steric strain between the three bulky *tert*-butyl groups in the C_3 structure. This steric strain is reduced in the C_1 structure as the three *tert*-butyl groups undergo torsional displacements of 18° against each other.

Referring to the thermochemical data reported in Table 3, it is seen that the G3(MP2) ΔH_{f298} values of tri-TBM with eq 1 and isodesmic schemes are −226.0 and −231.4 kJ mol^{-1}, respectively. These two values are in good agreement with the experimental value,[27] −235.2 ± 4.3 kJ mol^{-1}, with the isodesmic scheme yielding a better result. From this comparison, it is seen that, there is a small accumulation of systematic errors (about 5 kJ mol^{-1}) in this atomization scheme for this molecule. Therefore, eq 2 or 3 should be used to reduce the systematic errors. The two values generated by these two equations are −230.4 and −231.6 kJ mol^{-1}, respectively, which are nearly the same as that of the isodesmic scheme.

Before proceeding to tetra-TBM, it is pointed out that, as may be seen from Table 3, if we used the C_3 structure of tri-TBM to calculate its thermochemical data, the ΔH_{f298} values would be in the range 170−175 kJ mol^{-1}, very different from the experimental data. This piece of calculated energetics data is additional evidence that supports the C_1 structure for tri-TBM.

3.4. Tetra-*tert*-butylmethane (tetra-TBM). Tetra-TBM, a compound that has not yet been synthesized, is even more crowded around the central carbon atom than tri-TBM. In this work, both the T and T_d structures of tetra-TBM have been studied. The T_d structure is calculated to have 10 and 13 imaginary vibrational frequencies at the HF/6-31G(d) and MP2-(Full)/6-31G(d) levels, respectively, while the T structure has all real vibrational frequencies at both of these levels. Therefore, it may be concluded that the equilibrium structure of tetra-TBM has T symmetry. In Table 4, we compare the optimized bond lengths for the central C_t-C_q bonds (1.661 Å), the C_m-H_m bond (1.087 Å), and the $C_tC_qC_m$ angle (115.7°) of the optimized T structure at the MP2(Full)/6-31G(d) level with the spectroscopically determined force field (SDFF) results (1.683 Å, 1.074−1.088 Å, and 115.9°, respectively).[5] It is found that our results are in good agreement with the SDFF results except for the bond length of the C_t-C_q bond. It should be noted that the SDFF results were derived from the rather crude HF/6-31G level. Therefore, it is believed that our calculated central C_t-C_q bond (1.661 Å) should be more reliable than the SDFF result. Moreover, the C_t-C_q bond (1.661 Å) of tetra-TBM is the longest C−C bond found in the TBM molecules studied in this work. The lengthening of the innermost C−C bonds indicates the increase of strain from mono-TBM < di-TBM < tri-TBM < tetra-TBM. We also believe that tetra-TBM should have the longest C−C bond among the saturated hydrocarbon molecules.

Upon examining the structural data of unsaturated hydrocarbon compounds in the literature, it is found that the longest C−C bond length is 2.827 Å, found in $[Et_4N]_2[TCNE]_2$ (TCNE = tetracyanoethylene).[28] Less spectacularly, there are the long C−C bonds in 1,1,2,2-tetraphenyl-3,8-dibromobuta[*b*]naphthalene (1.712 Å), 1,1,2,2-tetraphenyl-3,8-diiodobuta[*b*]naphthalene (1.734 Å), and 1,1,2,2-(2,2′-biphenyl)-3,8-diiodobuta[*b*]naphthalene (1.724 Å).[29] There are also other examples with slightly shorter C−C bonds such as those with lengths of 1.652, 1.653, and 1.688 Å found in *trans*-1,2-dihydroxy-1,2-bis(*p*-tolyl)-acenaphthene,[30] (4*R*,*S*,5*RS*)-4-chloro-3-phenyl-1,7-dioxa-2-aza-spiro(4.4)non-2-en-6-one,[31] and hexahydro-1,2-dimethyl-3,6-pyridazinedione,[32] respectively. The last cited examples have bond lengths that are comparable to the longest C−C bonds found in the present work, 1.661 Å in tetra-TBM.

Examining the geometry of the T structure of tetra-TBM more closely, we have found that the inner five carbon atoms retain the idealized T_d structure. However, inclusion of the outer 12 methyl carbon atoms (but NOT the hydrogens) already reduces the symmetry of the aggregate to T. It is interesting to note that the central C_t-C_q bond of the T_d structure of tetra-TBM is 1.723 Å, which is longer than that of the T structure (1.661 Å). This difference is due to the large steric strain among the four bulky *tert*-butyl groups in the T_d structure of tetra-TBM. This steric strain is reduced in the T structure as the four *tert*-butyl groups undergo torsional displacements of 16° against each other.

Referring to the thermochemical data reported in Table 3, it is seen that the G3(MP2) ΔH_{f298} values of tetra-TBM with use of eq 1 and isodesmic schemes are −133.7 and −140.9 kJ mol^{-1}, respectively. From the experience of our study of tri-TBM, we believe the isodesmic result should be more reliable. In any event, the accumulated systematic error is still relatively small, about 7 kJ mol^{-1}, and, based on the accuracy of the calculated results for mono-TBM, di-TBM, and tri-TBM, the error range for the isodesmic ΔH_{f298} for tetra-TBM should be within ±10 kJ mol^{-1}. The two values generated from eqs 2 and 3 are −139.5 and −141.1 kJ mol^{-1}, respectively. Once again, these two values are essentially the same as the result obtained by the isodesmic scheme.

4. Conclusion

Employing both the isodesmic and atomization schemes, the ΔH_{f0} and ΔH_{f298} for mono-TBM, di-TBM, tri-TBM, and tetra-TBM have been calculated by using the G3 and G3(MP2) models of theory. Upon examining the results, it is found that all of the calculated ΔH_{f298} values are well within ±10 kJ mol^{-1} of the available experimental data for the first three compounds.

Hence, for tetra-TBM, for which no experimental thermochemical data are available, the (isodesmic) G3(MP2) results reported in this work should be reliable estimates. Moreover, we found that the atomization scheme is marginally more suitable for the study of small molecules, while the isodesmic scheme is more suitable for the larger ones. Structurally, it is found that the equilibrium structures of mono-TBM, di-TBM, tri-TBM, and tetra-TBM have T_d, C_2, C_1, and T symmetry, respectively. In addition, the energy-minimized structure of each molecule is determined and all structural parameters are generally in good agreement with the available experimental data.[33] Finally, the innermost C−C bond lengths increase along the series mono-TBM < di-TBM < tri-TBM < tetra-TBM, a trend expected by considering the steric effect in these molecules.

Acknowledgment. The work described in this paper was supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region (Project No. CUHK4275/00P). We would like to thank Mr. Frank Ng and the High Performance Computing Support Team of Information Technology Services Center of The Chinese University of Hong Kong for their computing assistance. We are also grateful to Professor L. S. Bartell for helpful correspondences.

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(33) Note that the electron diffraction experimental bond lengths (which are averages over anharmonic molecular vibrations) are longer than the calculated bond lengths (which neglect effects of vibrations) and the differences to be expected are typically 0.008 Å for C−C bonds and 0.02 Å for C−H bonds. When these differences are taken into account, the agreement between theory and experiment becomes even better. See, for example, Bartell, L. S. *J. Chem. Phys.* **1955**, *23*, 1219.