

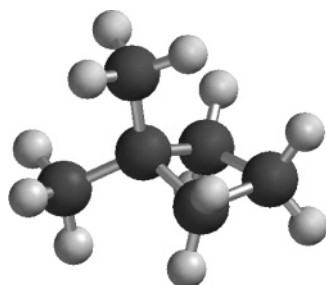
## Conventional Strain Energy in Dimethyl-Substituted Cyclobutane and the *gem*-Dimethyl Effect

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The *gem*-dimethyl effect is the acceleration of cyclization by substituents in the chain and is often used in organic synthesis as a ring-closing effect. Calculations on cyclobutane, methylcyclobutane, and 1,1-dimethylcyclobutane are performed. 1,1-Dimethylcyclobutane is a four-membered carbon ring with *gem*-dimethyl substituents. Optimum equilibrium geometries, harmonic vibrational frequencies, and corresponding electronic energies are computed for all pertinent molecular systems using SCF theory, density functional theory (DFT), and second-order perturbation theory (MP2) with two triple- $\zeta$  quality basis sets, 6-311G(d,p) and 6-311G+(2df,2pd). Additional single-point calculations are performed using the optimized MP2/6-311G+(2df,2pd) geometries and coupled-cluster theory including single and double excitations and noniterative, linear triple excitations (CCSD(T)). Calculations indicate that 1,1-dimethylcyclobutane is more than 8 kcal mol<sup>-1</sup> less strained than cyclobutane, that is, there is at least some thermodynamic component to the *gem*-dimethyl effect.

### I. Introduction

Cyclic compounds are noted for their reactivity and instability. Baeyer<sup>1</sup> described the causes of this instability in terms of molecular strain related to deviations from idealized bond angles. Other contributors to strain result from the stretching or compression of bond lengths,<sup>2</sup> bond eclipsing such that two regions of significant electron density overlap,<sup>3,4</sup> and the compression of van der Waals radii.<sup>5</sup> Taking into account only steric considerations, one might predict that cyclopropane is more strained than cyclobutane, since cyclopropane exhibits significantly greater bond angle compression.<sup>6–19</sup> However,

determinations of the strain energy of these two molecules conclude that the strain is quite similar.<sup>8,9,13,20,21</sup> This finding suggests that all stabilizing and destabilizing factors must be considered when determining the overall strain of a molecule, and Cox and Pilcher introduced the term “conventional strain energy”<sup>8</sup> to encompass all of these considerations.

In this study, we calculate the ring strain of several cyclic systems to study the *gem*-dimethyl effect, a synthesis technique which utilizes substitution of two methyl groups on an otherwise

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(1) Baeyer, A.; *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 2269.  
 (2) Westheimer, F. H. In *Steric Effects in Organic Chemistry*; Newman, M. S., Ed.; John Wiley: New York, 1956; p 523.  
 (3) Pitzer, K. S. *J. Chem. Phys.* **1937**, *5*, 469.  
 (4) Pitzer, K. S. *Science* **1945**, *101*, 672.  
 (5) Dunitz, J. D.; Schomaker, V. *J. Chem. Phys.* **1952**, *20*, 1703.  
 (6) Brown, H. C. *Rec. Chem. Prog.* **1953**, *14*, 83.  
 (7) Brown, H. C. *J. Chem. Soc.* **1956**, 1248.  
 (8) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970.  
 (9) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

(10) Hoffmann, R. *Tetrahedron Lett.* **1970**, 2907.  
 (11) Hoffmann, R.; Stohrer, W.-D. *J. Am. Chem. Soc.* **1971**, *93*, 6941.  
 (12) Radom, L.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 5935.  
 (13) Benson, S. W. *Thermochemical Kinetics*; John Wiley: New York, 1976.  
 (14) Deakne, C. A.; Allen, L. C.; Laurie, V. W. *J. Am. Chem. Soc.* **1977**, *99*, 1343.  
 (15) Greenberg, A.; Liebman, J. *Strained Organic Molecules*; Academic Press: New York, 1978.  
 (16) Durmaz, S.; Kollmar, H. *J. Am. Chem. Soc.* **1980**, *102*, 6942.  
 (17) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800.  
 (18) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3811.  
 (19) Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467.  
 (20) Cremer, D.; Kraka, E. In *Structure and Reactivity*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York, 1988; p 65.  
 (21) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Chemistry*; John Wiley & Sons: New York, 1994; pp 676–677.

unsubstituted carbon and leads to additional stability for a cyclic compound. This substitution aids in the cyclization reaction, and hinders ring opening once the cycle has been formed. There are several proposed kinetic explanations for this stabilization effect, but a thermodynamic effect, such as lowered ring strain, has not been considered. Cyclobutane, methylcyclobutane, and 1,1-dimethylcyclobutane, the latter of which has the *gem*-dimethyl substitution, were chosen so that the unsubstituted cyclic systems' strain could be compared to systems that were identical except for the addition of the dimethyl substitution.

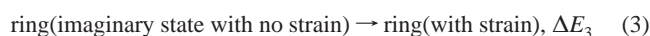
The *gem*-dimethyl effect, also called the *gem*-dialkyl effect, was first described in 1916 by Beesley, Ingold, and Thorpe.<sup>22</sup> The effect was noted when synthesis was attempted for certain three, four, and five member substituted rings. The rate of cyclization could be increased by adding the two methyl groups to a carbon adjacent to the reacting carbon, the carbon that would connect to the other end of the molecule in the cyclization reaction. Sometimes, a cyclic system could be formed when dimethyl substituents were added that could not be formed otherwise. These authors proposed a kinetic hypothesis to explain this effect stating that when the methyl substituents are added, the internal angle of the carbon is compressed bringing the reacting carbons closer together and making the cyclization reaction more likely. A more widely accepted kinetic hypothesis was proposed by Bruce and Pandit.<sup>23</sup> Their reactive rotamer hypothesis argues that the Thorpe-Ingold effect is only a small part of the *gem*-dimethyl effect, and that the much greater component involves the methyl substitutions affecting a larger number of *gauche* conformations (as opposed to *anti*-conformations). The steric hindrance introduced by the dimethylation makes the two conformations similarly strained, and there is a greater prevalence of *gauche* conformations compared to an unsubstituted system. In the *gauche* conformation, the reactive groups are in much closer proximity, and this favors the cyclization reaction.<sup>24,25</sup>

Several computational studies of ring strain exist in the literature. Alcamí et al. reported the conventional strain energies of the nine saturated three-membered ring systems composed of oxygen, nitrogen, and carbon.<sup>26</sup> The strain energy was computed within the homodesmotic model, and hyperhomodesmotic results were included for the three homocycles and for oxaziridine. Their study was limited, however, to a double- $\zeta$  valence basis set and to SCF frequencies for the determination of zero-point energy corrections. In addition, no correlation effects beyond those included in second-order perturbation theory were calculated, but correlation effects may be important in the calculation of conventional strain energy. In work by Lewis et al. on the isomers of oxaziridine, higher-order correlation effects were found to be important in the computation of the strain energy of those four-membered heterocyclic ring systems.<sup>27</sup> The effect of substituents on strain energies was examined by Bach and Dmitrenko<sup>28,29</sup> for a variety of small molecules. Specifically, the strain energy of cyclobutane and *gem*-dimethylcyclobutane, relative to cyclohexane was calcu-

lated using the G2 and G2(MP2) levels of theory. However, no direct comparison of these compounds to methylcyclobutane is made and few absolute strain energies are presented. Additionally, only one homodesmotic equation is considered for the systems studied, so the convergence of the model is not demonstrated. We look to extend this work in several important ways. The effect of higher-order correlation effects will be considered using both MP2 and CCSD(T) while employing triple- $\zeta$  valence quality basis sets, and several levels of the *s*-homodesmotic model will be used to determine the most efficient, accurate model.

## II. Computational Details

In the current study, the strain energy of cyclobutane, methylcyclobutane, and 1,1-dimethylcyclobutane were computed within the isodesmic,<sup>30,31</sup> homodesmotic,<sup>32</sup> and the hyperhomodesmotic<sup>33,34</sup> models. All three of these models may be grouped together within the *s*-homodesmotic model of Zhao and Gimarc<sup>35</sup> shown in eqs 1–3.



In eqs 1 and 2, A, B, and C are molecular units from the ring system each having a length of  $s+1$  non-hydrogen atoms; A', B', and C' are the same units with additional atoms from the ring added making them each length  $s+2$ . Note that  $\Delta E_3$ , the sum of  $\Delta E_1$  and  $\Delta E_2$ , equals the strain energy. However,  $\Delta E_1$  is zero because the hypothetical reaction breaks and forms the same bonds. Thus,  $\Delta E_2$  equals  $\Delta E_3$  which in turn equals the strain energy, and  $\Delta E_2$  can be computed via any standard quantum mechanical model. When the parameter  $s$  is equal to zero, the reaction described above conserves both the number and types of bonds. Such a reaction is said to be isodesmic.<sup>30,31</sup> When the parameter  $s$  equals one, the reaction conserves not only the number and types of bonds, but the valence environment around each atom as well; such reactions are homodesmotic.<sup>32</sup> For  $s$  equal to two, the bonding environments around adjacent atoms are also conserved; comparable reactions are said to be hyperhomodesmotic.<sup>33,34</sup>

To illustrate exactly what molecular systems must be considered in determining the ring strain within the *s*-homodesmotic model, eqs (4–6) give the appropriate reactions for cyclobutane.



The number of acyclic systems obviously increases when a branched system is considered. The reactions needed for computation of the ring strain for methylcyclobutane (eqs 7–9) and 1,1-

(22) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc. II* **1915**, 1080.

(23) Bruce, T. C.; Pandit, U. K. *J. Am. Chem. Soc.* **1960**, *82*, 5858.

(24) Jung, M. E.; Gervay, J. *J. Am. Chem. Soc.* **1991**, *113*, 224.

(25) Jung, M. E.; Kiankarimi, M. *J. Org. Chem.* **1998**, *63*, 2968.

(26) Alcamí, M.; M $\acute{o}$ , O.; Y $\acute{a}$ ñez, M. *J. Comput. Chem.* **1998**, *19*, 1072.

(27) Lewis, L. L.; Turner, L. L.; Salter, E. A.; Magers, D. H. *J. Mol. Struct. (Theochem)* **2002**, *592*, 161.

(28) Bach, R. D.; Dmitrenko, O. *J. Org. Chem.* **2002**, *67*, 2588.

(29) Bach, R. D.; Dmitrenko, O. *J. Org. Chem.* **2002**, *67*, 3896.

(30) Dill, J. D.; Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 6814.

(31) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley: New York, 1986; p 298.

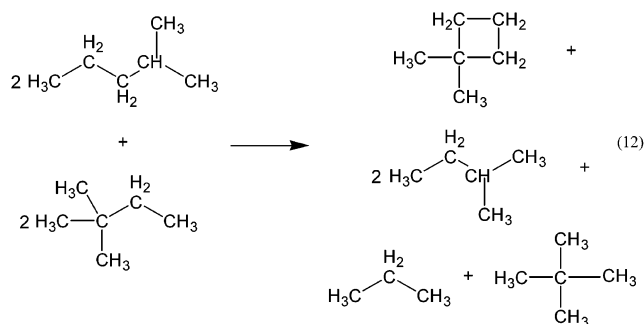
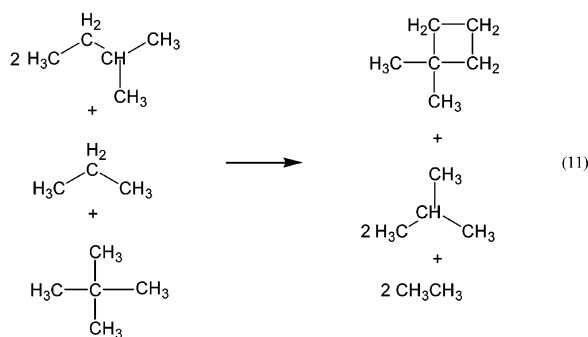
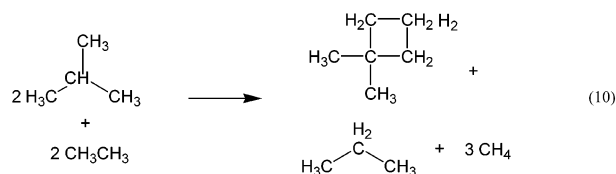
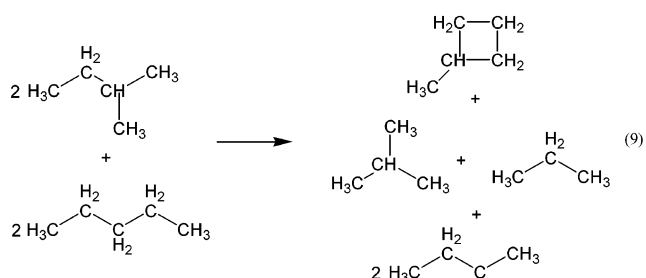
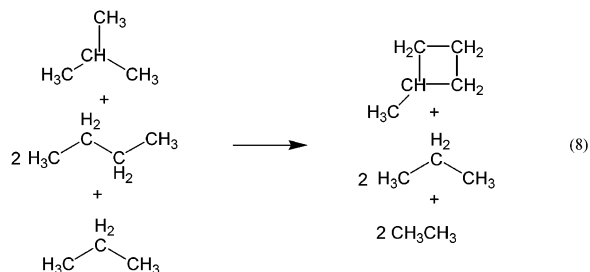
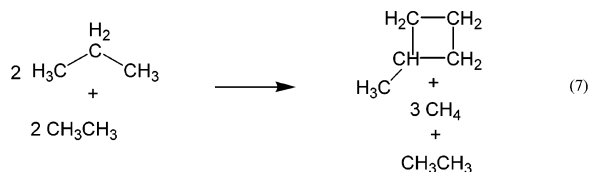
(32) George, P.; Trachtman, M.; Bock, C. W.; Brett, A. M. *Tetrahedron* **1976**, *32*, 317.

(33) Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 7500.

(34) Blahous, C. P., III; Schaefer, H. F., III *J. Phys. Chem.* **1988**, *92*, 959.

(35) Zhao, M.; Gimarc, B. M. *J. Phys. Chem.* **1993**, *97*, 4023.

dimethylcyclobutane (eqs 10–12) within the *s*-homodesmotic model are given below.



To obtain the energies for all the acyclic systems, optimum equilibrium geometries were computed for the singlet ground states

of all pertinent molecular systems using SCF theory, second-order perturbation theory (MP2),<sup>36</sup> and density functional theory (DFT).<sup>37–39</sup> The DFT functional employed was the B3LYP hybrid functional comprising Becke's three-parameter functional<sup>40</sup> using the LYP correlation functional.<sup>41,42</sup> Two basis sets, 6-311G(d,p)<sup>43</sup> and 6-311+G(2df,2pd),<sup>44,45</sup> both of triple- $\zeta$  quality on valence electrons, were employed. For all but the smallest molecules, numerous conformations were computed in order to ensure that the lowest energy conformation was obtained for each molecular system. For each conformation, harmonic vibrational frequencies were also calculated at the same level of computation to guarantee that each optimized geometry corresponds to a true local minimum and obtain the zero-point energy correction (ZPE). In all cases, electronic energies plus zero-point energies were used to compute the strain energies because the vibrational energies of the molecules are certainly included when strain energies are determined experimentally. Additionally, single-point energy calculations were performed using coupled-cluster theory including single and double excitations (CCSD)<sup>46,47</sup> and CCSD with inclusion of noniterative, linear triple excitations (CCSD(T))<sup>48,49</sup> at the optimized MP2/6-311+G(2df,2pd) geometry. All of these high-level correlated calculations employed the 6-311+G(2df,2pd) basis set. In all of the ab initio correlated calculations reported in this study core molecular orbitals (MOs) were frozen but no virtual orbitals deleted. All calculations were performed using the Gaussian98 program package.<sup>50</sup>

### III. Results and Discussion

The conventional strain energies determined with the 6-311G(d,p) and 6-311+G(2df,2pd) basis sets and including zero-point corrections are tabulated in Tables 1 and 2, respectively. Cyclobutane, methylcyclobutane, and 1,1-dimethylcyclobutane are compared to note the effect of the *gem*-dimethyl substitution. On comparing the SCF, B3LYP, and MP2 results for all three molecules a significant basis set effect is not noticed. Excluding the unreliable isodesmic model, results at any level of theory for any molecule are within 1 kcal mol<sup>-1</sup> for both basis sets. In general, the remaining discussion will focus on the results from

(36) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(37) Hohenberg, P.; Kohn, W. *Phys. Rev. B* **1964**, *136*, 864.

(38) Kohn, W.; Sham, L. J. *Phys. Rev. A* **1965**, *140*, 1133.

(39) Parr, R. G.; Yang, W. *Density-functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989.

(40) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(41) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(42) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(43) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

(44) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(45) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265.

(46) Cizek, J. *Adv. Chem. Phys.* **1969**, *14*, 35.

(47) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(48) Urban, M.; Noga, J.; Cole, S.; Bartlett, R. J. *J. Chem. Phys.* **1985**, *83*, 4041.

(49) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(50) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, J.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, M. S.; Pople, J. A. *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh PA, 1998.

**TABLE 1. Strain Energies (kcal mol<sup>-1</sup>) Determined Using 6-311G(d,p)**

	SCF <sup>a</sup>	B3LYP <sup>a</sup>	MP2 <sup>a</sup>
cyclobutane			
isodesmic	16.65	15.44	13.70
homodesmotic	23.43	23.31	25.83
hyperhomodesmotic	23.60	23.20	26.26
methylcyclobutane			
isodesmic	16.08	14.93	13.44
homodesmotic	21.98	21.62	25.09
hyperhomodesmotic	19.53	19.80	24.22
1,1-dimethylcyclobutane			
isodesmic	16.49	15.25	14.09
homodesmotic	19.11	19.35	23.99
hyperhomodesmotic	16.31	16.53	23.07

<sup>a</sup> Including ZPE correction.**TABLE 2. Strain Energies (kcal mol<sup>-1</sup>) Determined Using 6-311+G(2df,2pd)**

	SCF <sup>a</sup>	B3LYP <sup>a</sup>	MP2 <sup>a</sup>	ΔZPE	CCSD <sup>b</sup>	CCSD(T) <sup>b</sup>
cyclobutane						
isodesmic	16.45	15.08	13.40	-5.675	14.95	14.24
homodesmotic	23.36	23.15	26.46	-2.414	26.02	26.21
hyperhomodesmotic	23.67	23.07	27.43	-1.936	26.89	27.22
methylcyclobutane						
isodesmic	15.86	14.64	13.24	-5.408	14.73	14.06
homodesmotic	21.91	21.50	25.96	-2.239	25.36	25.66
hyperhomodesmotic	19.46	19.64	25.55	-2.019	24.55	25.19
1,1-dimethylcyclobutane						
isodesmic	16.29	15.05	13.83	-5.192	7.74	8.07
homodesmotic	18.88	18.99	24.80	-2.280	16.26	17.80
hyperhomodesmotic	16.06	16.31	24.27	-2.075	17.64	18.55

<sup>a</sup> Including ZPE correction. <sup>b</sup> Including MP2 ΔZPE correction.

the larger 6-311+G(2df,2pd) basis set since higher-order correlation calculations were performed only in this basis.

Since the CCSD(T) homodesmotic and hyperhomodesmotic models are convergent around the experimental strain energy of cyclobutane (26.3 kcal mol<sup>-1</sup>), an average of these two models will be taken as the conventional strain energy, yielding overall strain energies of 26.7, 25.4, and 18.2 kcal mol<sup>-1</sup> for cyclobutane, methylcyclobutane, and *gem*-dimethylcyclobutane. The MP2 average value of 26.9 kcal mol<sup>-1</sup> for cyclobutane is still a reasonable match; however, SCF (23.52) and DFT (23.11) both underestimate the strain. Typically, SCF overemphasizes the ionicity of the bonds, thereby predicting bonds to be shorter and stronger than they should be. In the s-homodesmotic model strain is computed as extra energy contained in the system over its bond energies. Therefore, SCF theory should generally underestimate the conventional strain, as we see in our results, where the SCF energy for cyclobutane is approximately 3 kcal mol<sup>-1</sup> to low. Again, this erroneous result is mirrored in the B3LYP results. Similar errors in computed B3LYP energies of hydrocarbons, and specifically alkanes, have been reported previously by others.<sup>51-53</sup>

A qualitative pattern of decreasing conventional ring strain with methyl substitution is seen at any level of theory. While MP2 typically matches the CCSD(T) results fairly well, there

(51) Pan, J.-W.; Rogers, D. W.; McLafferty, F. J. *J. Mol. Struct. (Theochem)* **1999**, *468*, 59.(52) Wodrich, M. D.; Corminboeuf, C.; Schleyer, P. v. R. *Org. Lett.* **2006**, *8*, 3631.(53) Schreiner, P. R.; Fokin, A. A.; Pascal, A. A., Jr.; Meijere, A. D. *Org. Lett.* **2006**, *8*, 3635.**TABLE 3. Optimized Geometric Parameters<sup>a</sup>**

geometric parameter & absolute energy	6-311+G(2df,2pd)		
	SCF	DFT	MP2
cyclobutane			
energy, au	-156.1465005	-157.2677482	-156.8373515
<i>r</i> <sub>e</sub> (CC), Å (ring)	1.54	1.55	1.54
∠HCH, deg (exterior)	108.48	108.42	109.14
∠CCC, deg (ring)	88.44	88.56	87.72
∠CCCC, deg	18.73	18.02	22.54
methylcyclobutane			
energy, au	-195.1964116	-196.598026	-196.0627731
<i>r</i> <sub>e</sub> (CC), Å (ring)	1.54	1.55	1.55
∠CC <sub>1</sub> H, deg (exterior)	109.58	109.71	110.65
∠HCH, deg (exterior)	108.49	108.49	109.20
∠CC <sub>1</sub> C, deg (ring)	88.13	88.16	87.53
∠CC <sub>3</sub> C, deg (ring)	88.29	88.44	87.66
∠C <sub>1</sub> CC <sub>3</sub> , deg (ring)	88.57	88.73	87.97
∠CCCC, deg	19.01	18.32	22.23
1,1-dimethylcyclobutane			
energy, au	-234.2439708	-235.9261923	-235.2892575
<i>r</i> <sub>e</sub> (CC), Å (ring)	1.55	1.56	1.55
∠CC <sub>1</sub> C, deg (exterior)	110.61	110.77	110.93
∠HCH, deg (exterior)	108.33	108.41	109.14
∠CC <sub>1</sub> C, deg (ring)	88.03	87.97	87.63
∠CC <sub>3</sub> C, deg (ring)	88.73	88.90	88.11
∠C <sub>1</sub> CC <sub>3</sub> , deg (ring)	89.42	89.49	88.73
∠CCCC, deg	15.83	15.39	19.51

<sup>a</sup> C<sub>1</sub> is the methyl- or dimethyl-substituted carbon. C<sub>3</sub> is the carbon across the ring from the substituted carbon.

is a notable exception for 1,1-dimethylcyclobutane, where higher-order correlation better describes the nonbonded interactions of the two methyl groups found in the *gem*-dimethylated molecule. The thermodynamic component of the *gem*-dimethyl effect is most clearly illustrated by the CCSD(T) results, where methylcyclobutane is only 1.3 kcal mol<sup>-1</sup> less strained than cyclobutane and 1,1-dimethylcyclobutane is 7.2 kcal mol<sup>-1</sup> less strained than methylcyclobutane. The overall difference in strain between cyclobutane and 1,1-dimethylcyclobutane is 8.5 kcal mol<sup>-1</sup> at the CCSD(T) level. This difference is similar to the 7.3 kcal mol<sup>-1</sup> difference reported by Bach and Dmitrenko when they considered the strain energies of these two systems relative to cyclohexane (25.6 kcal mol<sup>-1</sup> for cyclobutane and 18.3 kcal mol<sup>-1</sup> for 1,1-dimethylcyclobutane). However, the strain energy they report for 1,1-dimethylcyclobutane using a homodesmotic equation (the method most similar to our calculations) is 23.7 kcal mol<sup>-1</sup>, significantly higher than our CCSD(T) estimate of 18.2 kcal mol<sup>-1</sup> and closer to our MP2 result of 24.5 kcal mol<sup>-1</sup>.

The geometric parameters of the optimized equilibrium geometry were analyzed to offer possible explanations for the trends in conventional strain energy that were just discussed. The results are given in Table 3. The notation used in the tables uses the term exterior to describe angles whose vertex is an atom in the cycle and endpoints are atoms not in the cycle. The term ring is used to describe angles whose vertex and endpoints are all atoms in the cycle. The angle denoted CCCC at the bottom of the table is the dihedral angle that gives the degree of nonplanarity of the cyclic system. Notations regarding the numbering of the atoms in the cycle are included at the bottom of the table. The effect of dimethylation was noticed in the decreasing conventional strain energy for cyclobutane, methylcyclobutane, and 1,1-dimethylcyclobutane. A comparison of these molecules' geometries shows a noticeable geometric difference with the dimethyl substitution.

Every level of calculation shows that as methyl groups are substituted for hydrogens, the exterior bond angle between these substituents and the carbon of the cycle increases. For example,



at the MP2/6-311+G(2df,2pd) level of calculation the exterior HCH bond angle in cyclobutane was 109.14°. At the same level of calculation, the exterior CCH bond angle for methylcyclobutane was 110.65° and the exterior CCC bond angle in 1,1-dimethylcyclobutane was 110.93°. The increase in the value of this exterior bond angle is coupled with changes in interior angles of the ring. The interior angle in which the carbon bonded to the methyl group(s) lies at the vertex decreases with methyl substitution from its value in cyclobutane (87.72°). Yet, this decrease is not systematic, as this angle is larger in 1,1-dimethylcyclobutane (87.63°) than in methylcyclobutane (87.53°). However, both of the two interior angles adjacent to this initial interior angle do increase systematically and to a larger degree with methyl substitution: 87.72° in cyclobutane, 87.97° in methylcyclobutane, and 88.73° in 1,1-dimethylcyclobutane. We believe that this relief in Baeyer strain may be one of the primary reasons that the overall conventional strain energy is reduced with methyl substitution.

Finally, it is interesting to note that the ring becomes less puckered with methyl substitution as indicated by the decrease in the dihedral angle of the ring. This decrease may be necessary to relieve increased steric strain caused by the larger substituent.

#### IV. Conclusions

1,1-Dimethylcyclobutane is more than 8 kcal mol<sup>-1</sup> less strained than cyclobutane due to the stabilization afforded by *gem*-dimethyl substitutions. This suggests that the *gem*-dimethyl

effect has a thermodynamic component that has not been previously considered. The lowering of conventional strain energies is a product of the cyclization reaction, not the reactants, and therefore differs from the reactive rotamer hypothesis, which invokes a kinetic argument based on the relative stabilities of various configurations of the reactants. The lowering of conventional strain energies with the addition of *gem*-dimethyl substitutions is a property that should be evident in other systems.

We found conventional strain energy calculations to be more dependent on electron correlation rather than basis sets effects, so it should be acceptable to use optimized geometries from smaller basis sets to perform single-point calculations with higher levels of theory. SCF and B3LYP both underestimate the strain energy. MP2 agrees with experiment in most cases, but methods employing higher-order correlation effects, such as CCSD(T), are required to determine accurately the strain energy for molecules with significant nonbonded interactions.

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**Supporting Information Available:** Electronic energies for all molecular systems included in this study and  $\alpha$ -matrices for MP2-optimized structures containing six carbon atoms. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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