How Accurate Are Approximate Methods for Evaluating Partition Functions for Hindered Internal Rotations?

Ching Yeh Lin, Ekaterina I. Izgorodina,[†] and Michelle L. Coote*

ARC Centre of Excellence for Free Radical Chemistry and Biotechnology, Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia

The accuracy of several low-cost methods (harmonic oscillator approximation, CT-Cω, SR-TDPPI-HS, and TDPPI-HS) for calculating one-dimensional hindered rotor (1D-HR) partition functions is assessed for a test set of 644 rotations in 104 organic molecules, using full torsional eigenvalue summation (TES) as a benchmark. For methods requiring full rotational potentials, the effect of the resolution at which the rotational potential was calculated was also assessed. Although lower-cost methods such as Pitzer's Tables are appropriate when potentials can be adequately described by simple cosine curves, these were found to show large errors (as much as 3 orders of magnitude) for non-cosine curve potentials. In those cases, it is found that the TDPPI-HS method in conjunction with a potential compiled at a resolution of 60° offers the best compromise between accuracy and computational expense. It can reproduce the benchmark values of the partition functions for an individual mode to within a factor of 2; its average error is just of a factor of 1.08. The corresponding error in the overall internal rotational partition functions of the molecules studied is less than a factor of 4 in all cases. Excellent cost-effective performance is also offered by CT-Cω, which requires only the geometries, energies, and frequencies of the distinguishable minima in the potential. With this method the geometric mean error in individual partition functions is 1.14, the maximum error is a modest 2.98 and the resulting error in the total 1D-HR partition function of a molecule is less than a factor of 5 in all cases.

1. Introduction

An important application of computational chemistry is the a priori prediction of thermochemistry. However, this entails the calculation of partition functions to relate the electronic structure information generated by ab initio molecular orbital calculations to the enthalpies and entropies of molecules at some nonzero temperature. The partition function (Q) serves as a bridge between the quantum mechanical states of a system and its thermodynamic properties and is given by the formula

$$Q = \sum_i g_i \exp\left(-\frac{\epsilon_i}{k_B T}\right) \qquad (1)$$

In this equation, k_B is the Boltzmann constant and the ϵ_i values are the energy levels of the system, each having a number of degenerate states g_i, as obtained by solving the Schrödinger equation at the specified temperature T. In theory, this equation should be solved for all active modes but in practice the calculations are greatly simplified by making a number of approximations. In particular, the partition function is usually separated into the product of the translational, rotational, vibrational and electronic terms. This approximation is generally considered to be valid, provided the reaction takes place on a single electronic surface. Simple analytical expressions for these separate terms can then be obtained, provided one further assumes that the reacting species are ideal gas molecules that satisfy the rigid rotor/harmonic oscillator approximation. The

＊ Corresponding author. Fax: 61 2 6125 0750. Email: mcoote@rsc.anu.edu.au.
† Current address: School of Chemistry, Monash University Box 23, Victoria 3800, Australia.

resulting equations, which are frequently implemented in computational chemistry software packages, allow one to calculate the partition functions and associated thermodynamic properties of a molecule at a given temperature on the basis of its geometry, frequencies, and electronic state.

The accuracy of computational thermochemistry depends not only on the accuracy of the electronic-structure calculations but also on the validity of the approximations used in calculating the partition functions. Although most of the above approximations are reasonable, at least for gas-phase reactions occurring on a single electronic surface, the use of the harmonic oscillator approximation can be a potentially large source of error. For example, in radical addition to C=S double bonds, the use of the harmonic oscillator approximation can cause one to underestimate the equilibrium constant by as much as 2 orders of magnitude,[1] and significant errors have also been reported for many other systems, including the thermochemistry of *n*-alkanes[2] and propagation rate coefficients in free-radical polymerization.[3] The errors arise because the harmonic oscillator approximation assumes that, for each normal mode, the potential field associated with the molecule's distortion from the equilibrium geometry is a parabolic well. Though this is reasonable for bond stretching motions, many of the low-frequency torsional modes would be more appropriately treated as hindered internal rotations. Unfortunately, there is no simple analytical solution to the Schrödinger equation for the case of a hindered internal rotation, and, moreover, the numerical solution requires the calculation of the full rotational potential for each relevant mode. As a result, the correct treatment of the low-frequency torsional modes can add considerably to the computational cost of the calculations, especially for larger molecules. The development

Partition Functions for Hindered Internal Rotations

J. Phys. Chem. A, Vol. 112, No. 9, 2008 **1957**

of low-cost methods for predicting the hindered internal rotational partition functions is highly desirable.

To reduce the computational cost of obtaining partition functions, we have four main options available to us: (1) reducing the level of theory of the electronic structure calculations themselves; (2) reducing the dimensionality of the problem by ignoring coupling between modes; (3) reducing the number of points at which the potential energy surface is evaluated; (4) simplifying the solution of the Schrödinger equation. With regard to option 1, it is clear that identifying cost-effective accurate methods for calculating the geometries, frequencies, and rotational potentials is crucial. However, because the performance of computational methods is often very system-specific, a general evaluation of this factor is beyond the scope of the present work. Nonetheless, it is worth noting that the type of electronic structure information normally required to calculate partition functions (geometries, frequencies and rotational potentials) can usually be obtained with a sufficiently high degree of accuracy at much lower levels of theory than are required for studying the energetics of reactions due to the greater degree of systematic error cancellation.[4] For the types of species studied in the present work, assessment studies[5] have indicated that low levels of theory such as B3LYP/6-31G(d) are usually adequate for calculating the geometries, frequencies, and partition functions, provided transition structures are corrected to a higher level of theory via an IRCmax[6] technique.

With regard to option 2, in the present work we ignore coupling between internal modes altogether and restrict ourselves to one-dimensional hindered rotor (1D-HR) problems. This approximation is made necessary by the large size of the molecules under study. Although even a well-implemented 1D-HR model is potentially subject to error, a large part of this error can be mitigated by choosing an appropriate method for combining the hindered rotor partition for the specific mode with the harmonic oscillator partition functions for the remaining vibrational modes. For example, Van Cauter et al.[7] have shown that excellent results are possible if one applies the harmonic oscillator approximation to all $3N - 6$ internal modes of a molecule, and then multiplies the resulting vibrational partition function by a correction factor for each internal hindered rotor partition function. This factor is then calculated as the ratio of the 1D-HR partition function to the corresponding "pure" vibrational partition function, as calculated from second derivative of the rotational potential. Using approximations such as this, the 1D-HR model has been shown to provide reasonable results in situations where testing against more sophisticated treatments is possible.[8]

On the basis of the 1D-HR model, in the present work we examine whether further simplifications through (3) and (4) can be achieved without compromising the accuracy of the results obtained. A wide range of approximate methods for solving the 1D-HR problem have been developed, varying both in the amount of electronic structure information required and in the manner in which the Schrödinger equation is solved. The most accurate require a full rotational potential for the relevant mode, use this to solve numerically the Schrödinger equation for a one-dimensional rigid rotor, and then obtain the partition function via eigenvalue summation as in eq 1. Even using this approach, further savings are possible if one can increase the step size at which the potential is evaluated. In the extreme case, by assuming that the rotational potential follows a simple cosine curve with a known symmetry number σ, it is possible to obtain the entire rotational potential on the basis of the calculated

rotational barrier. Moreover, for this special case, the well-known Pitzer Tables[9] contain tabulated numerical solutions to the 1D-HR problem, and the requirement of solving the one-dimensional rigid rotor Schrödinger equation can also be avoided. More generally, Truhlar and co-workers have derived several simple analytical formulas of varying accuracy for evaluating the partition function on the basis of the electronic structure information available. Their simplest method, called CT-Cω, requires only the geometry and frequencies of the distinguishable minima on the internal rotational potential;[10] at the other extreme, the TDPPI-HS method, evaluates the partition function on the basis of the entire rotational potential.[11] Further details for several of these methods are provided in the following section.

Recently, Ellingson et al.[11] evaluated a number of the available methods for calculating hindered rotor partition functions for the case of H_2O_2. On the basis of this study they recommended that, if a full internal rotational potential is available, TDPPI-HS offered an accurate alternative to the full tosional eigenvalue summation (TES) approach. Alternatively, when the energies at all of the stationary points (i.e., local minima and transition structures) of the internal rotational potential surface are available, SR-TDPPI-HS was the most efficient method. In cases where only the geometries and frequencies of the distinguishable minima were available, CT-Cω was the preferred option.[10] In the present work, we examine the applicability of these results to the internal rotational modes of a large test set of organic molecules including various types of C−C, C−O, C−S rotations. We compare the accuracy of TDPPI-HS, SR-TDPPI-HS, CT-Cω, and the Pitzer Tables against the TES approach for a 1D-HR. We also compare the results with those obtained under harmonic oscillator (HO) approximation. For those methods requiring full rotational potentials, we also examine whether the use of a resolution of 60° instead of the customary 10° has a large impact on the accuracy of the results.

2. Theoretical Procedures

In the present work, 1D-HR partition functions were calculated using five different methods of varying accuracy and computational expense for a test set of 644 rotations in 104 organic molecules. The corresponding harmonic oscillator partition functions were also calculated for purposes of comparison. The most accurate 1D-HR methods required full rotational potentials for the relevant modes, and these were evaluated as relaxed scans at two different resolutions, 60° and 10°. The electronic-structure information (rotational potentials, geometries and frequencies) needed to evaluate the partition functions was obtained at a consistent level of theory, B3-LYP/6-31G(d), and were taken largely from earlier studies involving the reactions of these molecules.[12] Electronic-structure information for the remainder were calculated using the same software, GAUSSIAN 03,[13] and the same procedures, B3-LYP/6-31G-(d), as in these earlier studies. Our assessment studies[5] have shown that this simple level of theory provides excellent approximations to the geometries and rotational potentials of the types of molecular species in our test set. In the present work, we use this information (or the relevant subsets of it) to calculate the partition functions for the various modes at 298.15 K using the alternative methods so that the performance of the lower-cost methods can be assessed. The calculations were carried out using an in-house program called T-Chem.[14] The methods used for calculating the partition functions are described below; Table 1 summarizes the relative costs of the studied

TABLE 1: Relative Cost of Alternative 1D-HR Methods for Different Symmetry Numbers (σ)

method	electronic structure information[a]			partition function calculation[b]
	$\sigma = 1$	$\sigma = 2$	$\sigma = 3$	
HO	1	1	1	1
CT-Cω	P[c]	P[c]	P[c]	1
Pitzer Tables	2	2	2	1
SR-TDPPI-HS	2P	2P	2P	1
TDPPI-HS 60°	6	3	2	1
TDPPI-HS 10°	36	18	12	1
TES 60°	6	3	2	86400
TES 10°	36	18	12	86400

[a] Number of points on the rotational potential for which optimized geometries are required. *P* is the number of distinguishable minima on the rotational potential energy surface (the total number of minima *M* is given by the product, σP). In the present work, when implementing SR-TDPPI-HS, we look for a maximum of three distinguishable minima when $\sigma = 1$, and one when $\sigma = 2$ or 3. [b] Relative amount of CPU time required to perform the partition function calculation (assuming all necessary electronic structure data is already available) on a on 2 GHz G5 Mac PowerPC. [c] Although only *P* points are required in this calculation, frequency calculations are required in addition to geometry optimizations and energy calculations.

methods with respect to both the electronic structure information required and the calculation of the partition function from this information.

TES. At our benchmark level of theory, 1D-HR partition functions were calculated by solving the eigenvalues of the one-dimensional Schrödinger eq 2 for a rigid rotor.

$$-\frac{\hbar^2}{2I_r}\frac{d^2\Psi}{d\theta^2} + V(\theta)\Psi = \epsilon_i\Psi \qquad (2)$$

In this equation Ψ is the wavefunction, ϵ is the energy, I_r is the reduced moment of inertia, and $V(\theta)$ is the rotational potential. As noted above, at our benchmark level of theory, $V(\theta)$ was calculated as a relaxed scan through 360° in steps of 10°. The resulting potential was then fitted with a Fourier series of up to 18 terms and evaluated at a resolution of 1.2°. The reduced moment of inertia (I_r) is assumed to be independent of θ and was calculated from the optimized geometry using the equation for $I^{(2,3)}$, as defined by East et al.[15] Equation 2 was converted into the Hill differential equation to solve for the eigenvalues, ϵ, using the program T-Chem.[14] The resulting energy levels ϵ_i were then summed to obtain the partition function Q^{TES}, as follows:

$$Q^{TES} = \frac{1}{\sigma}\sum_i \exp\left(-\frac{\epsilon_i}{k_BT}\right) \qquad (3)$$

where σ is the symmetry number associated with that rotation.

It should be noted that there are two different conventions in use in the literature for reporting the partition functions for the internal modes. In the first, the zero of energy is taken as the "bottom of the potential well"; in the second, "$V = 0$", the zero of energy is taken as the first vibrational level. The resulting partition functions that are calculated under the alternative conventions differ by the zero-point vibrational energy. In the "bottom of the potential well convention" zero-point energy is included in the 1D-HR partition function of each individual mode; in the "$V = 0$" convention, the total zero-point vibrational energy of the molecule is calculated separately, and added to the 0 K energy barrier or enthalpy of the reaction. Because the

Pitzer Tables use the "$V = 0$" convention,[9] we have adopted this for the present work. Thus, in the TES method, the energy levels are corrected so that the first energy level is set as the zero of energy, prior to summing them, as in eq 3. However, the TDPPI-HS, SR-TDPPI-HS, and CT-Cω methods of Truhlar and co-workers[10,11] have been designed to follow the "bottom of the potential well" convention. As a result, the partition functions obtained under these methods need to have the zero-point vibrational energy removed from them, so that they can be compared with the partition functions calculated under the TES and Pitzer Tables methods. To do this, we have included the inverse of the zero-point vibrational energy, ZPE^{-1}, as a pre-factor in their respective formulas.

$$ZPE^{-1} = \exp\left(\frac{\hbar\omega_e}{2k_BT}\right) \qquad (4)$$

where ω_e is the frequency of the mode at the equilibrium geometry. It will be seen that, for simplicity, the ZPE has been calculated under the harmonic oscillator approximation, whereas when built into the TDPPI-HS, SR-TDPPI-HS and CT-Cω formulas it is effectively calculated as a hindered internal rotation. However, unlike the overall partition function, the differences in the ZPE as calculated under the various alternative methods are very small and are not expected to affect the comparisons made.

TDPPI-HS. The TDPPI-HS method was developed by Truhlar and co-workers[11] as a simpler alternative to TES for cases where the full one-dimensional rotational potential is known. It uses the displaced points path integral (DPPI) method applied in one dimension only to the torsional degree of freedom (TDPPI) with harmonic sampling (TDPPI-HS). The partition function is given by

$$Q^{TDPPI-HS} = \exp\left(\frac{\hbar\omega_e}{2k_BT}\right)\frac{\sqrt{2\pi I_r k_B T}}{h} \times$$
$$\int_0^{2\pi/\sigma}\exp\left\{-\frac{1}{2k_BT}\left[V\left(\theta + \frac{c}{2}\right) + V\left(\theta - \frac{c}{2}\right)\right]\right\}d\theta \quad (5)$$

As noted above, we have introduced the pre-factor, $\exp(\hbar\omega_e/2k_BT)$ to remove the contribution from zero point vibrational energy so that the partition function follows the "$V = 0$" convention and can be compared directly with the TES and Pitzer Table methods. In the present work, the reduced moment of inertia, I_r, is calculated using the equation for $I^{(2,3)}$, as described previously[15] and is thus identical to the value used in the TES benchmark calculations. The rotational potential is also the same as the one used in the TES calculation, $V(\theta)$, but the torsional angle is shifted by a constant, $c/2$, which depends on the temperature (T), the reduced moment of inertia (I_r), and frequency at the equilibrium geometry (ω_e) as follows:

$$c = \left[\frac{8k_BT}{\omega_e^2 I_r}\ln\left(\frac{\sinh(\hbar\omega_e/2k_BT)}{\hbar\omega_e/2k_BT}\right)\right]^{1/2} \qquad (6)$$

The frequency at the equilibrium geometry, ω_e, is derived from the second derivative of the potential $V(\theta)$.

$$k = \frac{d^2V(\theta)}{d\theta^2}\bigg|_{\theta=\theta_e} \qquad \omega_e = \sqrt{\frac{k}{I_r}} \qquad (7)$$

SR-TDPPI-HS. The SR-TDPPI-HS method has been designed by Truhlar and co-workers[11] for situations in which the

Partition Functions for Hindered Internal Rotations

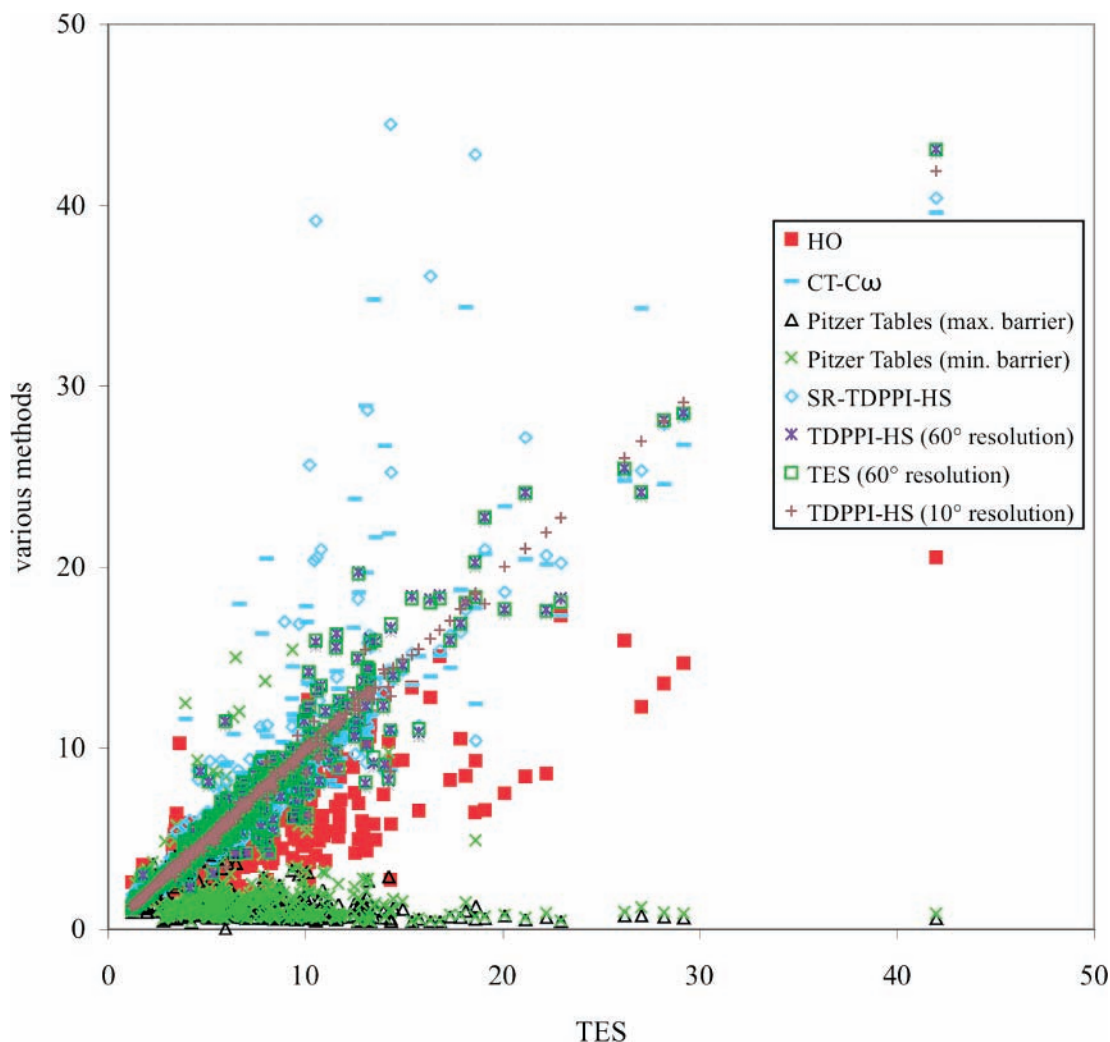*J. Phys. Chem. A, Vol. 112, No. 9, 2008* **1959**

Figure 1. Correlation between the benchmark TES 10° ID-HR partition functions and the various low-cost methods examined.

geometries and energies at *all* stationary points (i.e., local minima and transition structures) in the potential energy surface are known, in addition to the energy, geometry, and frequencies of the equilibrium structure. Once the energies of the stationary points are obtained, the segmented reference (SR) approximation is used to fit the rotational potential between each peak and minimum using a simple cosine function. The potential can be written as

$$V(\theta) = \sum_{j}^{P} \frac{(W_j^L - W_j^R)}{4}[1 - \cos M(\theta - \theta_j)] + U_j \quad (8)$$

where W_j^L and W_j^R are the left and right barrier and U_j is the energy at the *j*th distinguishable minimum of the rotation. Here, P is the number of distinguishable minima and M is the total number of minima in the range $[0, 2\pi]$. The only difference between this method and TDPPI-HS scheme is the potential used in the scheme. Therefore, the partition function $Q^{SR-TDPPI-HS}$ is also calculated using eq 5 but $V(\theta)$ is calculated using (8) rather than the full one-dimensional rotational potential.

Because SR-TDPPI-HS only requires the stationary points on the rotational potential, this method usually requires substantially less structure–reactivity information than the TES and TDPPI-HS methods except when the full potentials required for these latter methods are calculated at coarse resolutions.

However, for complicated potentials (which may contain a large number of distinguishable minima) it may in practice be difficult to identify all of the stationary points in rotational potential without first calculating the entire rotational potential at a fine resolution. Because this would completely sacrifice the computational advantage of the SR-TDPPI-HS method, in the present work we have tested a pragmatic version of this method in which we limit the number of stationary points that are sought on the basis of the nature of the rotating bonds. Thus, for rotations involving sp^M centers, a maximum of M minima (and M associated transition structures) are sought. As a result, the computational cost of this method (in terms of the electronic-structure information required) is the same as that of the TDPPI-HS and TES methods, when these latter methods are applied using a rotational potential compiled at a 360°/2M step size. In the present work, this means that for rotations involving sp^3 centers, the cost is the same as the 60° resolution TDPPI-HS and TES methods; for sp^2 centers the cost of SR-TDPPI-HS is slightly lower.

Pitzer Tables. When the rotational potential follows a simple cosine curve, it is possible to generate the entire potential on the basis of the rotational barrier and symmetry number. This greatly reduces the amount of electronic-structure information required to evaluate the partition function: instead of calculating the geometry and energy at 35 points (for the customary step size of 10°) on rotational potential energy surface in addition

TABLE 2: Maximum (MAX) and Geometric Mean (GM) Deviations of the Calculated 1D-HR Partition Functions from the Benchmark Values (TES 10°) for the Rotations in the Test Set[a]

method	methyl rotations[b]		non-methyl rotations[c]		total[d]	
	MAX	GM	MAX	GM	MAX	GM
HO	2.84	1.16	5.25	1.36	5.25	1.28
CT-Cω	1.39	1.13	2.98	1.14	2.98	1.14
Pitzer Tables (max. barrier)	1.20	1.02	296.60	4.79	296.60	2.73
Pitzer Tables (min. barrier)	1.22	1.02	48.52	4.26	48.52	2.54
SR-TDPPI-HS	1.10	1.02	5.70	1.17	5.70	1.12
TDPPI-HS (60° resolution)	1.10	1.02	1.97	1.12	1.97	1.08
TES (60° resolution)	1.08	1.01	1.94	1.12	1.94	1.08
TDPPI-HS (10° resolution)	1.08	1.03	1.73	1.02	1.73	1.02
TES (10° resolution)	1	1	1	1	1	1

[a] The errors in a calculated partition function were defined as the ratio of the calculated value to the benchmark 10° TES value, with numerator and denominator chosen such that the ratio was greater than or equal to one. [b] The subset of 233 methyl rotations. [c] The subset of 411 non-methyl rotations. [d] The complete test set of 644 rotations.

to equilibrium structure, it is only necessary to calculate one additional point, the rotational transition state. In such cases, the partition function can be calculated using a tabulated numerical solution to one-dimensional Schrödinger equation, known as the Pitzer Tables.[9] To use the Tables, one requires the barrier height of the potential and the inverse of the partition function of free rotor, Q^{FR}, which is defined in.

$$Q^{FR} = \frac{\sqrt{2\pi I_r k_B T}}{\hbar \sigma} \qquad (9)$$

In practice few rotational potentials can be adequately described by simple cosine curves. Nonetheless, it is of interest to determine the extent to which this assumption compromises the accuracy of the calculated partition functions for typical types of rotational modes. Clearly, when the rotational potential does not follow a simple cosine curve, selecting an appropriate value for the rotational barrier, so as to best approximate the potential as a cosine curve, can be problematic. In the present work, we have thus chosen the highest energy barrier to rotation throughout the entire potential. In practice, if one were to calculate single rotational transition structure, one would not necessarily locate the maximum barrier to rotation. We have thus also performed the analysis using the lowest rotational barrier throughout the entire potential. Consideration of these two extremes should provide a guide to the possible level of error in the results.

CT-Cω. The other low-cost method for evaluating the hindered-rotor partition function that is tested in the present work, CT-Cω,[10] requires the geometry and the frequencies at all of the distinguishable minima. Thus, when the potential follows a simple cosine curve it requires less structure–reactivity data than the Pitzer Tables; for more complicated potentials it requires slightly more, according to the number of distinguishable minima. For a given potential, the method requires information on only half the data points required by SR-TDPPI-HS; however, unlike SR-TDPPI-HS, the frequencies as well as energies are required at each optimized geometry. As in the case of SR-TDPPI-HS, we have set a pragmatic limit on the number of distinguishable minima that are sought for nonregular

potentials. Thus, for rotations involving sp^M centers, a maximum of M minima are sought.

Under the CT-Cω method, the partition function is evaluated via

$$Q^{CT-C\omega} = Q^{MC-HO} \tanh\left(\frac{Q^{FR}}{Q^I}\right) \qquad (10)$$

where Q^{FR} is the partition function of free rotor and is given by eq 9 above, Q^{MC-HO} is the multiconformer harmonic partition function and is given by eq 11 and Q^I is the intermediate partition function for intermediate temperature region and is given by eq 12. The frequency, ω_j, is obtained from electronic

$$Q^{MC-HO} = \sum_{j=1}^{P} \frac{\exp(-U_j/k_B T)}{1 - \exp(-\hbar\omega_j/k_B T)} \qquad (11)$$

$$Q^I = \sum_{j=1}^{P} \frac{\exp(-U_j/k_B T)}{\hbar\omega_j/k_B T} \qquad (12)$$

structure calculations at jth minimum of the rotation, and U_j is the local minimum at jth minimum of the rotation. As explained above, to follow the "$V = 0$" convention, the ZPE contribution has been removed from eq 11.

HO. The corresponding partition function for each internal rotational mode in the test set was also calculated under the harmonic oscillator approximation (HO), the default procedure in most computational chemistry software packages. This was done to allow us to compare the errors incurred in using approximate methods for calculating the partition function with those associated with doing nothing at all and retaining the harmonic oscillator calculations. Under the harmonic oscillator approximation, the partition function associated with an individual vibrational mode under the "$V = 0$" convention is given by

$$Q^{HO} = \frac{1}{1 - \exp\left(-\dfrac{\hbar\omega}{k_B T}\right)} \qquad (13)$$

where ω is the harmonic frequency. In the present work, we calculate the HO partition function using the frequency estimated from the second derivative of the rotational potential at the equilibrium structure via eq 7. As noted above, recent work[7,8] suggests that, when coupling between modes is not dealt with explicitly, this is the most appropriate manner in which to estimate the contribution of a internal rotational mode to the total partition function under the HO approximation so that it can then be corrected using the corresponding 1D-HR value.

3. Results and Discussion

To evaluate the accuracy of lower-cost methods for calculating 1D-HR partition functions, we considered a test set of 644 rotations in 104 organic molecules. The test set is described in full in the Supporting Information and comprised a variety of different C–C, C–O, and C–S rotations in both open- and closed-shell molecules including aromatic and aliphatic hydrocarbons, halides, esters and dithioesters, and involving a range of functional groups. For each rotation in the test set, 1D-HR partition functions were calculated via the five methods described above (CT-Cω, Pitzer's tables, SR-TDPPI-HS, TDPPI-HS, and TES), and the corresponding value of the partition function under the harmonic oscillator approximation (HO) was
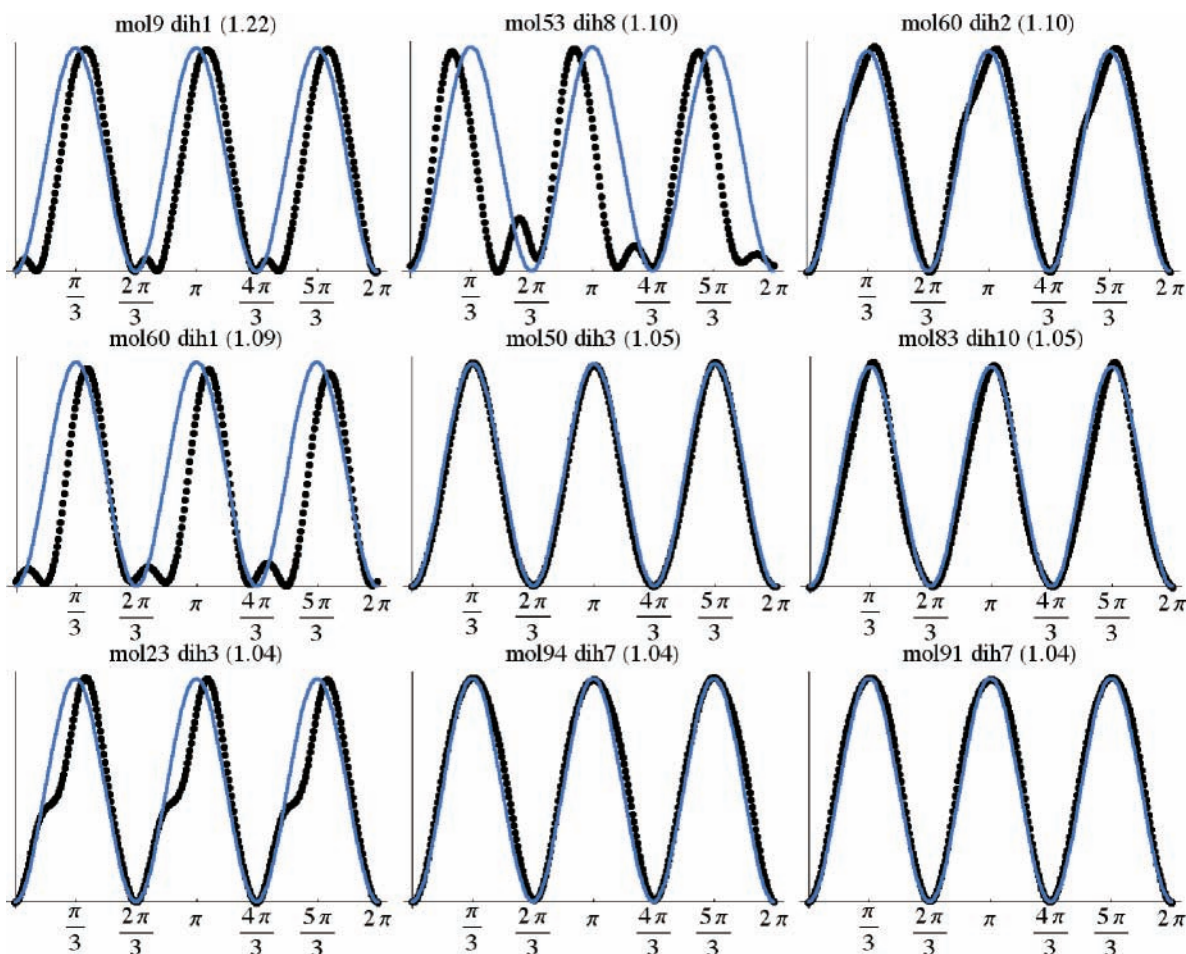
Partition Functions for Hindered Internal Rotations

J. Phys. Chem. A, Vol. 112, No. 9, 2008 **1961**

Figure 2. Methyl rotational potentials for which the deviations from the Pitzer Tables exceed a factor of 1.03 (deviations shown in brackets). The potential compiled at 10° resolution is shown in black; the corresponding cosine fit based on the rotational barrier and symmetry number is shown in blue. Structure and dihedral numbers are defined in Figure S1 of the Supporting Information.

also calculated for purposes of comparison. For the methods requiring full rotational potentials, TES and TDPPI-HS, the rotational potential was obtained for two different step sizes, 10° and 60°. The resulting individual values of the partition function at the various levels of theory are plotted against the corresponding benchmark data in Figure 1; the corresponding numerical values are provided in Table S1 of the Supporting Information.

From Figure 1, it is seen that there is a wide variation in the 1D-HR partition functions calculated via the alternative methods. Only the 10° TDPPI-HS values, which require the same electronic-structure information as the benchmark values, appear to show close agreement with the benchmark 10° TES values. The 60° TDPPI-HS and TES values show reasonable agreement with the benchmark data, though with increased scatter. This is also true of SR-TDPPI-HS and CT-Cω, though in these cases there are some significant outliers with much larger errors. The Pitzer Tables generally underestimate the benchmark data and appear to show larger errors than those incurred under the harmonic oscillator approximation, though there are several exceptional cases where the errors are much smaller.

To facilitate a more quantitative analysis of the results, the errors in the lower-cost methods (versus the TES 10° benchmark values) were estimated and are summarized in Table 2. Because the partition function contributes to the calculated rate or equilibrium constant in a multiplicative manner, errors in the partition function Q_i were calculated as the ratio of Q_i to the corresponding benchmark TES value, with the numerator and denominator chosen such that the ratio was always greater than

1. The overall error for the test set was then calculated as the geometric mean (GM),

$$\text{GM} = \left(\prod_{i=1}^{n} x_i\right)^{1/n} \quad \begin{cases} x_i = \dfrac{Q_i^{\text{TES}}}{Q_i} & \text{for } Q_i < Q_i^{\text{TES}} \\[2mm] x_i = \dfrac{Q_i}{Q_i^{\text{TES}}} & \text{for } Q_i > Q_i^{\text{TES}} \end{cases} \tag{14}$$

where n is the number of rotations in the test set. Because the performance of many of the methods tested is likely to be affected by how well the rotational potential can be described by a simple cosine curve, the geometric mean errors are also calculated separately for the 233 methyl rotations in the test set (as these might be expected to have rotational potentials that can be approximated by a simple cosine curve), and for the remaining 411 rotations (which would be expected to have more complicated rotational potentials). The results are now discussed in turn.

Methyl Rotations. If we examine first the subset of 233 methyl rotations, we note that the errors in all of the alternative methods are relatively small. This is not surprising. All of the methods examined (with the exception of HO and CT-Cω) should in principle be exact when compared with the benchmark TES values if the potential follows a cosine curve *exactly*. For most of the methyl rotations in the test set, the rotational potentials do follow a simple cosine curve, and the errors are thus negligible. For some of the rotations studied there are small
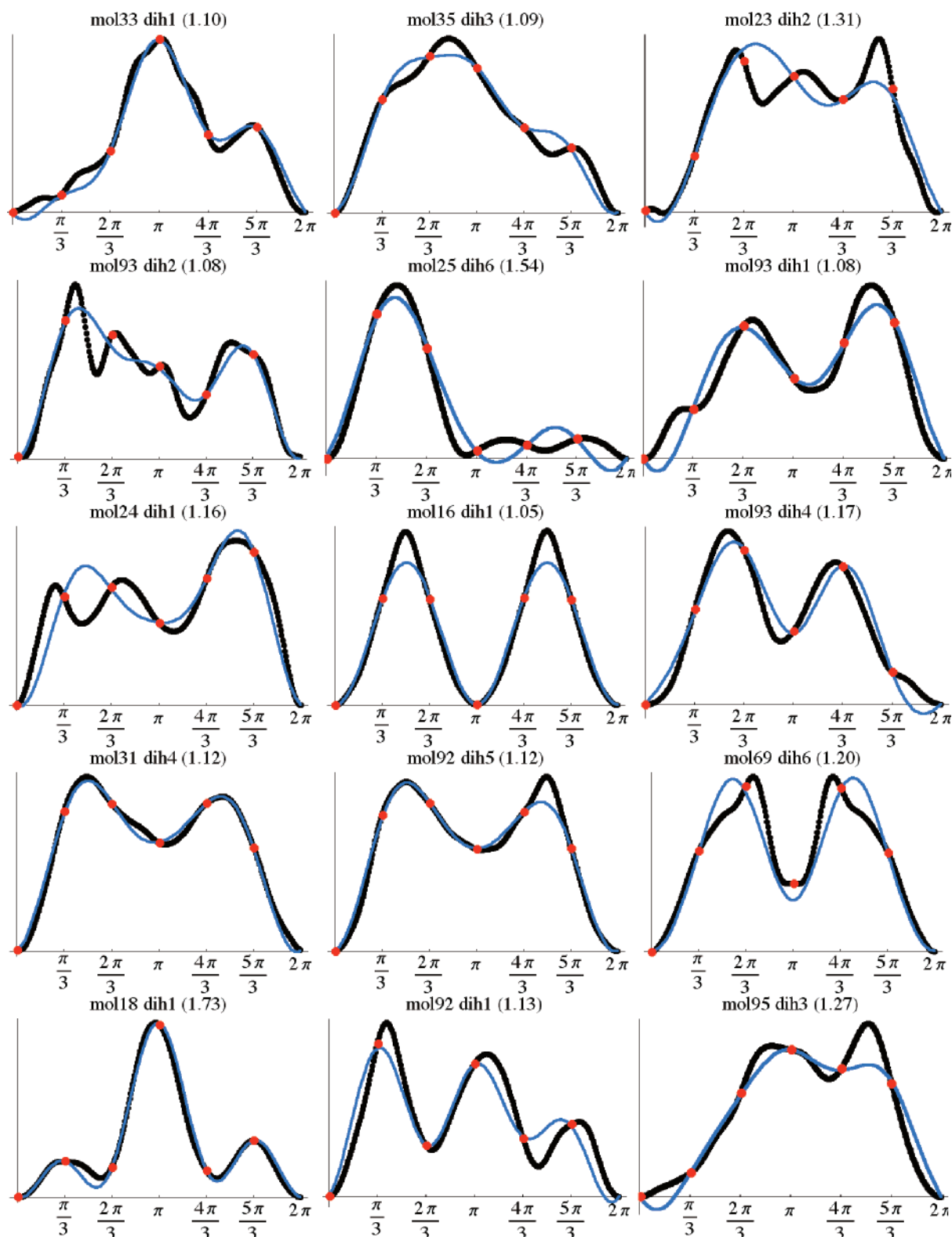
Figure 3. Typical rotational potentials from test set, as interpolated at 10° resolution and 60° resolution (red dots fitted by blue line). The deviations of the 1D-HR partition functions estimated under the TES method from the 60° potential, compared with the corresponding values under the more accurate 10° potential are shown in parentheses. Structure and dihedral numbers are defined in Figure S1 of the Supporting Information.

deviations from this functional form (see Figure 2), and these deviations result in the errors observed. Nonetheless, the errors are modest and it is clear that even these cases, the Pitzer Tables are adequate. Perhaps more importantly, the results of Table 2 confirm that the lowest-cost 1D-HR method examined, CT-Cω, also offers a modest improvement over the harmonic oscillator approximation, despite requiring no additional electronic-

structure calculations for these types of potential. This method would thus be a cost-effective approach to modeling 1D-HR partition functions for simple cosine rotational potentials.

Non-Methyl Rotations. For the remaining test set of rotations, the rotational potential does not follow a simple cosine curve (see, for example, Figure 3), and the errors in the lower-cost methods are, not surprisingly, much larger. In

Partition Functions for Hindered Internal Rotations

J. Phys. Chem. A, Vol. 112, No. 9, 2008 **1963**

particular, regardless of how the rotational barrier is chosen, the Pitzer Tables lead to errors that are much greater than those incurred under the harmonic oscillator approximation, are thus best avoided. It would seem that, if the rotational potential is complicated, it is essential that further electronic-structure information is obtained so that it can be properly characterized.

The other 1D-HR methods tested (CT-Cω, SR-TDPPI-HS, TDPPI-HS, TES) do sample additional points on the rotational potential and perform much better. Not surprisingly, the best results were obtained using the methods requiring the full rotational potential (i.e., TDPPI-HS and TES). These methods had maximum errors of less than a factor of 2 and geometric mean errors of less than a factor of 1.12, even when applied using a 60° step size in the potential. At this step size they required the same number of data points as the SR-TDPPI-HS method (when $\sigma = 1$ or 3, they required one additional point when $\sigma = 2$) but were significantly more reliable. Compiling the rotational potential at a 60° resolution, in place of the customary 10°, offers a 6-fold saving in the amount of electronic-structure data required with minimal additional error in the resulting TDPPI-HS or TES partition functions. In the present work, this is true even when minor qualitative differences in the interpolated potential at 60° and 10° were apparent (see, for example, Figure 3) and would imply that the use of a 60° resolution could be adopted for most rotational potentials without significantly affecting the accuracy of the results. At this resolution, there is no significant difference in the accuracy of the TES and TDPPI-HS procedures, and the latter method, which requires fewer flops in its Fortran routine, would be preferred. When extremely accurate results are required, one would of course revert to a 10° step size in compiling the rotational potential. At that step size, the TDPPI-HS method occasionally deviates from TES by up to a factor of 1.7, and this level of error, though small, would not justify the additional computational expense entailed in obtaining the additional points on the rotational potential. In that situation, TES would then be preferred over the TDPPI-HS.

Of the lower-cost methods examined, CT-Cω, showed excellent performance and is thus promising as a low-cost method for larger molecules. This method out-performed SR-TDPPI-HS, despite requiring electronic-structure information on only half of the data points required by SR-TDPPI-HS. Its geometric mean error was just 1.14 (compared with 1.17 for SR-TDPPI-HS), and its the maximum error was just 2.98 (compared with 5.70 for SR-TDPPI-HS). For comparison, the geometric mean error under the harmonic oscillator approximation was 1.36, and the maximum error was of a factor of 5.25. It should be reiterated that for the more complicated potentials, such as many of those shown in Figure 3, the accuracy of SR-TDPPI-HS (and possibly also CT-Cω) could have been improved by obtaining *all* of the stationary points in the rotational potential instead of the 4 or 6 we opted for in the present work (according to whether the rotating bonds involved sp^2 or sp^3 centers). However, this would have sacrificed its computational advantage over the more accurate TDPPI-HS and TES methods, as it would then have been necessary to scan the entire rotational potential using a reasonably small step size to ensure that all of the stationary points were identified. It would thus appear that TDPPI-HS and TES, when applied at a 60° resolution, offers the best compromise between accuracy and computational expense when a high degree of accuracy is required. However, CT-Cω is promising as a lower-cost method for studying larger molecules.
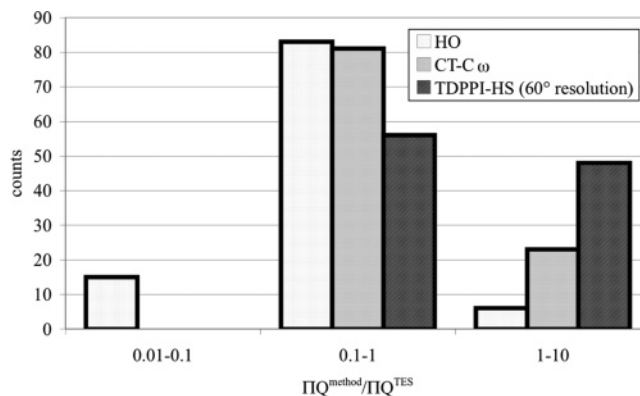

Figure 4. Histogram of the deviations of the total 1D-HR partition function from the TES 10° benchmark values under various approximate methods for each of the 104 molecules.

Practical Implications. It is clear that there is a wide variation in the accuracy of the lower-cost methods for calculating the 1D-HR partition functions, and to some extent this accuracy depends upon the type of rotation being studied. Given that the error in the partition function is multiplicative, and given that any given molecule may have several low-frequency torsional modes, it is of interest to examine the impact of these errors on the overall 1D-HR partition function for a molecule. To this end, for each molecule studied, we calculated the ratio of the product of its partition functions under a given approximate method to that calculated using the 10° TES method. We then compiled a histogram of the results for the entire test set (see Figure 4). The analysis was carried out for the 60° TDPPI-HS method, which appeared to show the best compromise between accuracy and computational expense, and the CT-Cω method, which is promising as a lower-cost method for larger molecules. The errors under the harmonic oscillator approximation are also shown for purposes of comparison.

From Figure 4 we find that the 60° TDPPI-HS method reproduces the total 1D-HR partition function of every molecule studied to within an order of magnitude. Indeed the maximum errors for this method were actually less than a factor of 4, and appear to be relatively random with approximately half of the molecules showing an underestimate and half showing an overestimate. What is encouraging is that the lower-cost method, CT-Cω, also reproduces the total 1D-HR partition function of every molecule studied to within a factor 5, despite requiring information for only half of the data points required by the 60° TDPPI-HS method. Not surprisingly, the harmonic oscillator approximation shows larger errors, with a small but significant portion of the molecules deviating by as much as 2 orders of magnitude. In general, both it and CT-Cω tend to underestimate the partition function, though for a small fraction of the molecules the total partition function is overestimated instead.

4. Conclusions

On the basis of our analysis of a test set of 644 rotations in 104 organic molecules, it would appear that, for simple methyl rotations, low-cost methods for calculating 1D-HR partition functions such as the Pitzer tables or CT-Cω offer an excellent approximation to compiling a high-resolution rotational potential and performing torsional eigenvalue summation (i.e., our benchmark 10° TES method).

For more complicated rotations, there is a greater variation in accuracy among the alternative methods with the Pitzer Tables in particular showing very large errors. Methods that utilize the entire rotational potential are required to obtain highly accurate

Lin et al.

results; however, significant computational savings are possible, if the potential is compiled using a 60° step size, rather than the customary 10°, and the TDPPI-HS method is used to evaluate the partition function, in place of TES. Using this method, the partition function of an individual mode in our test set can be reproduced to within a factor of 2 (with a geometric mean error of just 1.08); the total 1D-HR partition for a molecule can be reproduced to within a factor of 4.

Excellent cost-effective performance is also offered by CT-Cω, which requires only the geometries, energies and frequencies of the distinguishable minima in the potential. With this method the geometric mean error in individual partition functions is 1.14, the maximum error is a modest 2.98 and the resulting error in the total 1D-HR partition function of a molecule is less than a factor of 5 in all cases.

Supporting Information Available: A description of the test set, a full listing of the calculated partition functions and related information for each rotation, and relevant B3-LYP/6-31G(d) optimized geometries and rotational potentials. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Coote, M. L. *J. Phys. Chem. A* **2005**, *109*, 1230−1239.

(2) Vansteenkiste, P.; Van Speybroeck, V.; Marin, G. B.; Waroquier. M. *J. Phys. Chem. A* **2003**, *107*, 3139−3145.

(3) See, for example: (a) Heuts, J. P. A.; Gilbert, R. G.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 18997−19006. (b) Huang, D. M.; Monteiro, M. J.; Gilbert, R. G. *Macromolecules* **1998**, *31*, 5175−5187. (c) Van Cauter, K.; Van Speybroeck, V.; Vansteenkiste, P.; Reyniers, M.-F.; Waroquier, M. *Chem. Phys. Chem.* **2006**, *7*, 131−140. (d) Izgorodina, E. I.; Coote, M. L. *Chem. Phys.* **2006**, *324*, 96−110.

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

(5) See, for example: (a) Coote, M. L.; Wood, G. P. F.; Radom, L. *J. Phys. Chem. A* **2002**, *106*, 12124−12138. (b) Coote, M. L. *J. Phys. Chem. A* **2004**, *108*, 3865−3872. (c) Gómez-Balderas, R.; Coote, M. L.; Henry, D. J.; Radom, L. *J. Phys. Chem. A* **2004**, *108*, 2874−2883.

(6) Malick, D. K.; Petersson, G. A.; Montgomery, J. A. *J. Chem. Phys.* **1998**, *108*, 5704−5713.

(7) Van Cauter, K.; Van Speybroeck, V.; Vansteenkiste, P.; Reyniers, M.-F.; Waroquier, M. *Chem. Phys. Chem.* **2006**, *7*, 131−140.

(8) See, for example: Vansteenkiste, P.; Van Neck, D.; Van Speybroeck, V.; Waroquier, M. *J. Chem. Phys.* **2006**, *124*, 044314.

(9) (a) Pitzer, K. S.; Gwinn, W. D. *J. Chem. Phys.* **1942**, *10*, 428−440. (b) Pitzer, K. S. *J. Chem. Phys.* **1946**, *14*, 239−243. (c) Li, J. C. M.; Pitzer, K. S. *J. Phys. Chem.* **1956**, *60*, 466−474. (d) Kilpatrick, K. E.; Pitzer, K. S. *J. Chem. Phys.* **1949**, *17*, 1064−1075.

(10) Truhlar, D. G. *J. Comput. Chem.* **1991**, *12*, 266−270.

(11) Ellingson, B. A.; Lynch, V. A.; Mielke, S. L.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 084305.

(12) (a) Feldermann, A.; Coote, M. L.; Stenzel, M. H.; Davis, T. P.; Barner-Kowollik, C. *J. Am. Chem. Soc.* **2004**, *126*, 15915−15923. (b) Coote, M. L.; Izgorodina, E. I.; Cavigliasso, G. E.; Roth, M.; Busch, M.; Barner-Kowollik, C. *Macromolecules* **2006**, *39*, 4585−4591. (c) Izgorodina, E. I.; Coote, M. L. *Chem. Phys.* **2006**, *324*, 96−110. (d) Coote, M. L.; Izgorodina, E. I.; Krenske, E. H.; Busch, M.; Barner-Kowollik, C. *Macromol. Rapid Commun.* **2006**, *27*, 1015−1022. (e) Lin, C. Y.; Coote, M. L.; Petit, A.; Richard, P.; Poli R.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 5985−5994.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision B.03; Gaussian, Inc.: Pittsburgh, PA, 2003.

(14) This program is available at http://rsc.anu.edu.au/~mcoote/T-Chem.php.

(15) East, A. L. L.; Radom, L. *J. Chem. Phys.* **1997**, *106*, 6655.