JCTC Journal of Chemical Theory and Computation

Accurate Treatment of Energetics and Geometry of Carbon and Hydrocarbon Compounds within Tight-Binding Model

Alexander A. Voityuk*

Institució Catalana de Recerca i Estudis Avançats, Institute of Computational Chemistry, Universitat de Girona, 17071 Girona, Spain

Received February 16, 2006

Abstract: We show that a simple noniterative tight-binding model can provide reliable estimates of energetics and geometries of molecules with C−C and C−H bonds. The mean absolute error in heats of formation, ∼4.6 kcal/mol, is essentially smaller than those found in previous tight-binding schemes. The internal consistency of the calculated heats of formation enables the reliable prediction of bond dissociation energies and isomerization enthalpies. The model gives accurate molecular geometries of hydrocarbons; the mean absolute errors in bond lengths and bond angles are 0.015 Å and 1.4°, respectively. The calculated vibration frequencies agree reasonably well with experimental values. The method has proven to be transferable to complex carbon and hydrocarbon systems. The good performance of the model and its computational efficiency make it promising for simulations of carbon and hydrocarbon systems.

Introduction

While ab initio and DFT quantum chemical methods are widely used in molecular modeling, these techniques become inapplicable for extended systems containing hundreds of atoms, because of huge computational demands. Therefore, much less demanding semiempirical neglect of diatomic differential overlap (NDDO) methods are widely used for the quantum chemical treatment of such systems.[1] The schemes modified neglect of diatomic overlap (MNDO),[2] AM1,[3] PM3[4], and MNDO/d[5] have been proven to give accurate estimates of ground-state energetics. New semiempirical NDDO models have been recently developed.[6,7] In many cases, the results of semiempirical calculations are of the same quality as those of DFT calculations. Very recently, it has been shown that introducing the overlap matrix into the secular equations for MNDO-like methods leads to more accurate results.[8] This study provides a new direction for the development of semiempirical NDDO schemes.

In the past three decade, tight-binding (TB) schemes have also been widely applied to a variety of chemical systems.[9,10] The use of the parametrized TB approach for exploring the electronic properties of molecules and crystals was suggested in the seminal work of Slater and Koster.[11] The TB models, which bear a close similarity to the extended Hückel method,[12] are computationally even more efficient than the semiempirical NDDO schemes. The limiting step of the semiempirical calculations of extended systems is the diagonalization of the Hamiltonian matrix. Usually, a single-point calculation requires about 20 iterations; it means that 20 diagonalizations of the Fock matrix are needed for a closed-shell system, and 40 such steps are required when an open-shell system is treated using the spin-unrestricted method. Unfortunately, the number of iterations for the self-consistent treatment of π-conjugated systems such as carbon nanotubes may remarkably increase with the size of the model. In such situations, the semiempirical calculations become very time-consuming. However, when a noniterative tight-binding method is used, only two matrix diagonalizations (for the Hamiltonian and overlap matrixes) are needed independent of whether a closed- or an open-shell system is considered. Therefore, the noniterative TB approach can be applied to systems containing up to a few thousand atoms. The models are intensively used in dynamic simulations of nanostructures.

Two approaches are employed to determine TB parameters. One is based on DFT calculations and usually referred

* Fax: 34 972418356. E-mail: alexander.voityuk@icrea.es.

Carbon and Hydrocarbon Compounds

J. Chem. Theory Comput., Vol. 2, No. 4, 2006 **1039**

to as DFTB.[13,14] The DFTB method has been used for simulations of biological molecules, organic reactions, and nanostructures (see refs 15−18 and references therein). However, the performance of DFTB remains still not very clear, because no systematic assessment of the scheme has been published yet. Alternatively, the effective TB Hamiltonian can be parametrized using experimental data.[19−25] While the semiempirical TB models allow one to obtain reasonable molecular geometries, the calculated heats of formation and reaction energies are found to be not very accurate. A typical error in atomization energies (and in formation enthalpies) of hydrocarbons is in the range of 30−50 kcal/mol, and therefore, it is too large as compared with those of the standard semiempirical methods. The main reason for the large errors is that the TB schemes have been parametrized with respect to the energetic and structural properties of various bulk phases. Also, this problem is closely related to the transferability of TB parameters and their dependence on the bonding environment of the systems.[26]

The purpose of the present work is to describe a new noniterative TB scheme for the accurate treatment of molecules with C−C and C−H bonds. The model is referred to as the PNTB (parametrized noniterative tight-binding) scheme. The number of parameters for the short-range repulsion term is kept as small as possible to estimate the inherent accuracy of the effective Hamiltonian. The paper is organized as follows. In section 2, we briefly outline the tight-binding method and define the effective Hamiltonian and the short-range repulsive potential employed in the model. In section 3, we consider the performance of the proposed model by comparing the PNTB results with both experimental values and other calculations. In section 4, we give conclusions and outline possible extensions of the model.

Method

Within the tight-binding model, the total energy of the system can be expressed as

$$E = \sum_i^{occ} n_i \epsilon_i + E_{rep} = \sum_i^{occ} \langle \psi_i | H | \psi_i \rangle + E_{rep} \qquad (1)$$

The first term, the electronic energy, is a sum of the orbital energies ϵ_i of all orbitals with the occupation number n_i. The second term is a short-range repulsion energy which is approximated by a sum of the interatomic potentials G_{AB} depending only on the distance between atoms A and B.

$$E_{rep} = \frac{1}{2} \sum_{A,B} G_{AB}(R_{AB}) \qquad (2)$$

The effective one-electron Hamiltonian H is represented in a minimal basis of atomic orbitals (AOs). Because the AO basis is nonorthogonalized, the orbital energies ϵ_i are obtained by solving the generalized eigenvalue problem

$$\sum_i (H_{\mu\nu} - \epsilon_i S_{\mu\nu}) c_{\nu i} = 0 \qquad (3)$$

The matrix elements of the Hamiltonian are defined as follows:

$$H_{\mu\mu} = U_\mu^A \qquad (4)$$

$$H_{\mu\nu} = \beta_{\mu\nu} S_{\mu\nu} \qquad (5)$$

Here, U_μ^A is the energy of an electron in AO φ_μ (μ = s, p, or d) at atom A, $\beta_{\mu\nu}$ is the resonance parameter which describes the two-center interaction of AOs μ and ν of atoms A and B, respectively.

$$\beta_{\mu\nu} = \beta_{\mu\nu}^{AB} \exp\left[-\frac{1}{2}(\lambda_A + \lambda_B)(R_{AB} - r_{AB}^0)\right] \qquad (6)$$

where $\beta_{\mu\nu}^{AB}$ and λ_A are adjustable parameters and r_{AB}^0 is a scaling constant.

The repulsive potential G_{AB} includes a number of terms of different physical natures (the core−core repulsion, a correction due to double counting of the two-electron interaction, and the exchange-correlation energy). A simple exponential function is often used to approximate the potential:

$$G_{AB} = C_{AB} \exp[-\delta_{AB}(R_{AB} - r_{AB}^0)] \qquad (7)$$

However, this function is unsuitable at small interatomic distances; at $R_{AB} = 0$, the potential remains finite instead of being infinite. Because at short distances the two-center matrix elements $H_{\mu\nu}$, eq 5, have large negative values, some computational problems may arise. We overcome the deficiency by using a scaling factor $\exp[^1/_2(r_{AB}^0/R_{AB} - 1)]$. Combining this factor with eq 7, one obtains

$$G_{AB} = C_{AB} \exp\left[-\delta_{AB}(R_{AB} - r_{AB}^0) + \frac{1}{2}(r_{AB}^0/R_{AB} - 1)\right] \qquad (8)$$

The resulting potential should satisfactorily describe the short-range part of G_{AB}.

In opposition to the DFTB model, where the Hamiltonian matrix elements and the overlap integrals are defined only in a certain range of R_{AB} and assumed to be zero beyond this range,[13] no such constraints are employed in our model. The overlap matrix for all atom pairs in eq 3 is calculated using Slater-type functions with exponents ζ_s and ζ_p for s and p AOs, respectively. The angular factors are determined by transformation of the atomic orbitals under rotation.[11]

Because the energy of isolated atoms is calculated as

$$E^A = \sum_\mu n_\mu U_\mu^A \qquad (9)$$

the total energy E of a system, eq 1, has a correct limit at large interatomic distances. The standard enthalpy of formation (at T = 298 K) is estimated as

$$\Delta H_f^0 = E - \sum_A E^A + \sum_A H_f^{0,298}(A) \qquad (10)$$

where $\Delta H_f^{0,298}(A)$ is the experimental heat of formation of atoms A. The zero-point energy and the enthalpy term to heat the molecule from T = 0 K to T = 298 K are implicitly taken into account when one fits the semiempirical param-

Table 1. Parameters in the PNTB Hamiltonian

atomic parameters			bond-type parameters			
parameter	H	C	parameter	H−H	C−H	C−C
U_s^A (eV)	−13.605	−16.960	β_{ss} (eV)	−21.100	−24.610	−27.535
U_p^A (eV)		−12.080	$\beta_{pp\sigma}$ (eV)			−21.596
ζ_s (au)	1.30	1.85	β_{sp} (eV)		−20.737	−24.5655[a]
ζ_p (au)		1.60	$\beta_{pp\pi}$ (eV)			−18.979
λ_σ (Å^{-1})	0.094	0.244	C_{AB} (eV)	1.043	0.963	0.903
λ_π (Å^{-1})		0.058	δ_{AB} (Å^{-1})	4.570	4.807	4.968

[a] $\beta_{sp} = \frac{1}{2}(\beta_{ss} + \beta_{pp\sigma})$.

eters to experimental $\Delta H_f^{0,298}$ values.[1] This approach is commonly used by the parametrization of semiempirical methods.

Parametrization. The parameters of the effective Hamiltonian and the repulsive potential G_{AB} were derived as follows. The parameter U_s for hydrogen was set to −13.605 eV (the negative of the ionization potential of the atom). The exponents ζ_s and ζ_p were fixed after preliminary test calculations. For the C−C pair, $\beta_{sp} = \frac{1}{2}(\beta_{ss} + \beta_{pp\sigma})$. The scaling constants r_{AB}^0 for H−H, C−H, and C−C were set to 0.75, 1.10, and 1.45 Å, respectively. Note that the parameters r_{AB}^0 were introduced just to obtain similar values of the $\beta_{\mu\nu}^{AB}$ and C_{AB} parameters for different atom pairs and may be excluded from the scheme. All other parameters were fitted using experimental data of $\Delta H_f^{0,298}$ and structural parameters for several standard molecules. The experimental heats of formation were adopted from the NIST Chemistry WebBook.[27] The bond lengths and bond angles as well as the references to original sources can be found in refs 2−4. The molecules in a training set were chosen to represent the most common bonding situations in hydrocarbons. A nonlinear least-squares method was used to optimize the semiempirical parameters. Several parametrization runs were carried out starting from different parameter values and using different training sets. The resulting parameters were tested in extensive survey calculations in order to choose the set which yields the most balanced results. Table 1 lists the final values of the parameters.

Results and Discussion

Heats of Formation. Table 2 contains the calculated and experimental heats of formation of several hydrocarbons which belong to different classes. A statistical evaluation for 83 molecules (see the Supporting Information) shows that the mean error is −0.6 kcal/mol (on average, the model slightly overestimated the stability of hydrocarbons) while the mean absolute error (MAE) is 4.6 kcal/mol. The corresponding errors of MNDO, AM1, and PM3 are 11.9, 11.0, and 7.7 kcal/mol, respectively. These large MAEs of the standard semiempirical schemes are mainly due to considerable overestimation of the heat of formation of C_{60} (see below); they are reduced to 9.2, 7.0, and 5.6 kcal/mol, respectively, when the fullerene is excluded from the statistics. It should be emphasized that reparametrization of the MNDO-like methods for just CH compounds will essentially improve their performance. As seen from Table 2, small deviations of the calculated values of ΔH_f are obtained for both short and long alkanes. The method also

well reproduces the heats of formation of branched-hydrocarbon sterically crowded molecules with adjacent methyl groups. Small errors are found for cyclic and bicyclic molecules, for compounds with double and triple bonds, as well as for conjugated systems. Reliable estimates of ΔH_f are also predicted for aromatic compounds and the fullerene C_{60}. However, for some "difficult" molecules such as cubane and adamantane, the model provides less satisfactory data (the deviations from experimental results are found to be about 24 and 17 kcal/mol, respectively). The calculated heats of formation of radicals are in very good agreement with experimental data.

PNTB shows a considerable improvement over related TB schemes.[19−25] While the method of Horsfield et al.[22] gives accurate values of atomization energies for small alkanes, the error linearly increases with the size of the molecules (~5 kcal/mol per CH_2 group) and becomes 18 kcal/mol for C_5H_{12}. Then, while that scheme provides good results for compounds with double bonds, it considerably (by ~20 kcal/mol) underestimates the stability of molecules with triple bonds.[22] The model of Zhao and Lu[25] overestimates atomization enthalpies with a mean absolute error of about 50 kcal/mol. The partial atomization enthalpy (the atomization enthalpy divided by the number of atoms in a molecule) can be calculated with PNTB with a MAE of ~0.5 kcal/mol, which is an order of magnitude smaller than the errors of the previous TB schemes.[19−25]

Rotation Barriers. The energy barrier in the torsional motion about a single C−C bond arises from the steric interaction between the third nearest-neighbor atoms. In Table 3, we compare PNTB barriers with experimental data and ab initio values.[28−31]

In ethane, the barrier is defined as the energy difference between eclipsed (D_{3h}) and staggered (D_{3d}) conformations. The experimental value of the rotational barrier is 2.9 kcal/mol. Usually, tight-binding schemes considerably underestimate rotational barriers; for instance, the model of Wang and Mak predicts free rotation of methyl groups in ethane.[21] The PNTB calculated barrier, 1.3 kcal/mol, is half as large as the experimental value and close to the AM1 and PM3 estimates, 1.2 and 1.4 kcal/mol, respectively. Similarly, the PNTB barriers in propane and propene are too low. However, PNTB well reproduces the relative energies of butadiene and styrene conformations; the results are remarkably better than the corresponding energies calculated with MNDO, AM1, and PM3. While the PNTB scheme predicts a twisted structure of biphenyl, the twist angle is underestimated; it is found to be 24° instead of 44°. Because of that, the calculated

Table 2. Comparison with Experimental Results of Heats of Formation Calculated with PNTB, in kcal/mol

molecules	PNTB	exptl	molecules	PNTB	exptl
hydrogen	−5.3	0.0	**cyclic**		
alkanes			cyclopropane	18.1	12.7
methane	−10.7	−17.8	cyclopropene	70.3	66.2
ethane	−16.6	−20.0	methylene-cyclopropane	48.5	47.9
propane	−22.7	−25.0	cyclobutane	1.2	6.8
N-pentane	−35.0	−35.1	cyclobutene	37.6	37.5
neopentane	−35.1	−40.2	cyclopentadiene	33.5	32.1
2,2,3,3-tetramethylbutane	−50.6	−56.2	cyclohexane, chair	−35.8	−29.5
N-decane	−65.7	−59.6	cyclohexene, half-chair	−6.3	−1.2
unsuturated			bicyclobutane	66.0	51.9
ethylene	12.6	12.5	*trans*-bicyclopropyl	40.7	30.9
propene	6.0	4.6	bicyclo[2.1.0]pentane	38.3	37.8
isobutene	−0.6	−4.0	adamantane	−48.9	−32.2
1,3-*trans*-butadiene	24.5	26.3	cubane	124.6	148.7
1,2-butadiene	34.6	38.8	**radicals**		
acetylene	46.1	54.5	methyl	39.6	34.8
propyne	39.1	44.2	ethyl	32.6	28.0
allene	40.7	45.4	*n*-propyl	27.0	24.0
aromatic			isopropyl	25.7	22.3
benzene	19.8	19.7	*n*-buthyl	20.5	18.0
fulvene	49.5	53.5	*s*-buthyl	19.7	17.0
styrene	33.2	35.3	*t*-buthyl	19.2	11.0
indene	40.7	39.1	vinyl	69.2	63.4
mesitylene	1.9	−3.8	HCC	114.7	123.0
naphthalene	35.5	35.9	allyl	38.9	39.0
azulene	62.0	73.5	phenyl	80.6	79.0
anthracene	53.6	55.2	benzyl	47.5	49.0
phenanthrene	49.3	49.0	cyclopropyl	76.3	66.9
biphenylene	102.4	100.5	cyclopentdienyl	59.0	58.0
fullerene C$_{60}$	630.5	634.8			

Table 3. Conformational Energies for Prototypical Molecules, in kcal/mol

molecule	conformation	PNTB	MNDO	AM1	PM3	exptl (ab initio)
ethane (staggered)	eclipsed	1.3	1.0	1.2	1.4	2.9[a]
propane (trans/trans)	cis/trans	1.4	1.2	1.3	1.5	3.3 (3.7)[a]
	cis/cis	2.9	2.8	3.0	3.2	8.8
propene (cis)	trans	0.6	0.2	0.6	0.6	2.0 (2.0)[b]
butadiene (trans)	cis	1.3	0.5	0.7	0.7	3.8 (3.6−4.1)[c]
	perpendicular	5.2	0.5	1.9	1.5	6.1 (4.9−6.1)
styrene (planar)	perpendicular	4.2	−1.4	1.4	1.4	3.0−3.3 (2.4−2.7)[c]
biphenyl (optimized)	twist angle	24°	90°	40°	0°	44° (44°)[d]
	planar	0.3	6.8	2.1	0.0	1.4 (3.1)
	perpendicular	3.1	0.0	1.1	1.0	1.6 (1.5)

[a] Ref 28. [b] Ref 29. [c] Ref 30. [d] Ref 31.

energy of the coplanar conformation is lower and the energy of the perpendicular structure is higher than the reference values (Table 3).

Bond-Dissociation Energies. In Table 4, we compare energies for 20 bond-breaking reactions. Because the PNTB scheme provides accurate ΔH_f values for both open- and closed-shell systems (Table 2), the experimental C−H and C−C bond enthalpies are well reproduced by the calculation. The MAE is found to be 3.4 kcal/mol. Thus, PNTB can be applied to modeling bond-breaking processes.

Isomerization Reactions. The variety of hydrocarbons is based on the ability of carbon atoms to form single, double, and triple bonds. The changes in the valence state of carbon

atoms are associated with remarkable variations of atomic energies. Therefore, enthalpies of isomerization reactions can be considered as good test data to assess the performance of a computational method. Table 5 lists the calculated and experimental energies for 10 isomerization reactions. The mean absolute error amounts to 3 kcal/mol. The maximum deviation of 10 kcal/mol is found for the transformation of propyne into cyclopropene. The performance of PNTB becomes better for larger systems. The comparison suggests that PNTB provides consistent estimates of ΔH_f across different classes of hydrocarbons.

Fullerenes. Because fullerenes and carbon nanotubes play an important role in nanotechnology, computational modeling

Table 4. Bond Dissociation Enthalpies, in kcal/mol

bond		PNTB	exptl
CH_4	$\rightarrow CH_3 + H$	102.4	104.7
C_2H_6	$\rightarrow C_2H_5 + H$	101.2	100.1
	$\rightarrow CH_3 + CH_3$	88.8	82.8
C_2H_4	$\rightarrow C_2H_3 + H$	108.6	103.1
C_2H_2	$\rightarrow C_2H + H$	120.6	120.6
C_3H_8	$\rightarrow n\text{-}C_3H_7 + H$	101.7	101.0
	$\rightarrow i\text{-}C_3H_7 + H$	100.5	99.4
	$\rightarrow C_2H_5 + CH_3$	95.0	87.9
C_3H_6	$\rightarrow C_3H_5 + H$	85.1	86.2
C_4H_{10}	$\rightarrow s\text{-}C_4H_9 + H$	100.8	99.2
	$\rightarrow n\text{-}C_4H_9 + H$	101.5	100.1
	$\rightarrow 2C_2H_5$	94.1	86.0
$i\text{-}C_4H_{10}$	$\rightarrow t\text{-}C_4H_9 + H$	100.1	95.2
	$\rightarrow s\text{-}C_3H_7 + CH_3$	94.3	89.2
$c\text{-}C_3H_6$	$\rightarrow c\text{-}C_3H_5 + H$	110.3	106.3
Ph-H	$\rightarrow Ph + H$	112.8	111.4
Ph-CH_3	$\rightarrow PhCH_2 + H$	85.8	89.0
	$\rightarrow Ph + CH_3$	106.3	101.7
Ph-C_2H_5	$\rightarrow PhCH_2 + CH_3$	79.1	76.9
	$\rightarrow Ph + C_2H_5$	105.4	99.9

Table 5. Enthalpies of Isomerization Reactions, in kcal/mol

Reactant		Product	PNTB	Exp.
	$\rightarrow$		1.6	1.3
	$\rightarrow$		31.7	22.0
	$\rightarrow$		-8.2	-8.5
	$\rightarrow$		2.0	4.0
	$\rightarrow$		31.6	23.5
	$\rightarrow$		4.9	2.7
	$\rightarrow$		5.6	7.0
	$\rightarrow$		-13.0	-10.1
	$\rightarrow$		20.3	19.6
	$\rightarrow$		7.2	10.8

Table 6. Calculated and Experimental Bond Lengths in C_{70}, in Å

			experimental[35]	
	PNTB	B3LYP6-31G*	ND	GED
R_{aa}	1.443	1.452	1.460	1.46
R_{ab}	1.386	1.397	1.382	1.388
R_{bc}	1.442	1.44	1.449	1.453
R_{cc}	1.378	1.389	1.396	1.386
R_{cd}	1.440	1.449	1.464	1.468
R_{dd}	1.429	1.434	1.420	1.425
R_{de}	1.409	1.421	1.415	1.405
R_{ee}	1.452	1.471	1.477	(1.538)

Table 7. Comparison of Relative Energies of Isomers of C_{30} and C_{32} Fullerenes, in kcal/mol

molecule	PNTB	B3LYP6-31G*[17]
$C_{30}\_1\ (C_{2v})^a$	45.0	55.6
$C_{30}\_2\ (C_{2v})$	6.5	4.0
$C_{30}\_3\ (C_{2v})$	0.0	0.0
$C_{32}\_1\ (D_2)$	54.4	60.3
$C_{32}\_2\ (C_2)$	44.4	65.5
$C_{32}\_3\ (D_{3d})$	58.4	73.9
$C_{32}\_4\ (C_2)$	22.2	26.0
$C_{32}\_5\ (D_{3h})$	71.0	78.3
$C_{32}\_6\ (D_3)$	0.0	0.0

^{a} The numbering of isomers is the same as in ref 17.

of the carbon nanostructures has attracted much attention. To assess the performance of PNTB for such systems, we carried out calculations of several fullerenes. Note that large dispersions among the experimental heats of formation of C_{60} and C_{70} are found.[32] For C_{60}, the PNTB calculated $\Delta H_f^{0,298}$, 630.5 kcal/mol, is close to the 634.8 kcal/mol adopted by NIST[27] while being 16 kcal/mol larger than the estimate obtained by Kolesov et al.[33] The B3LYP/6-31G* calculations predict $\Delta H_f^{0,298} = 618$ kcal/mol.[34] It should be noted that the standard semiempirical methods MNDO, AM1, and PM3 considerably underestimated the stability of C_{60}; the calculated $\Delta H_f^{0,298}$ values are 868.5, 972.6, and 811.0 kcal/mol, respectively. For C_{70}, PNTB gives 685 kcal/mol,

which is in reasonable agreement with the B3LYP estimate of 658 kcal/mol[34] and the experimental values 666 and 658 kcal/mol tabulated in ref 32.

Also, PNTB calculations provide reliable estimates for structural parameters of fullerenes. In C_{60}, there are two types of C–C bonds with lengths 1.39 and 1.44 Å. The PNTB values, 1.395 and 1.445 Å, are in excellent agreement. In C_{70} (D_{5h} symmetry), there are five circles of atoms labeled with a, b, c, d, and e from the capping pentagon to the equator.[35] Table 6 contains calculated and experimental bond lengths in C_{70}. As can be seen, the PNTB results are in good agreement with experimental and B3LYP data.

In Table 7, we compare relative energies of isomers of small fullerenes C_{30} and C_{32} calculated using the PNTB and B3LYP methods. Overall, the PNTB results agree satisfactorily with the B3LYP estimates. The PNTB energies are found to be similar to the data derived within the DFTB model.[17] Note that the PNTB scheme reproduces the B3LYP data more accurately than the AM1 and PM3 semiempirical methods.

Geometries. Molecular geometries of some selected hydrocarbons are listed in Table 8. A statistical evaluation of structural parameters calculated by PNTB for 30 hydrocarbons (see the Supporting Information) shows that the mean absolute error in bond lengths is 0.015 Å (100 comparisons). The method systematically underestimate the C–C bond lengths, resulting in a mean sign error of −0.012 Å. Reliable results are also obtained for bond angles—the mean absolute error is 1.4° for 31 comparisons. Thus, the geometries of hydrocarbons can be well predicted by the PNTB model.

Carbon and Hydrocarbon Compounds

J. Chem. Theory Comput., Vol. 2, No. 4, 2006 **1043**

Table 8. Geometries of Selected Molecules[a]

molecule	variable	calcd	exptl
hydrogen	H−H	0.760	0.741
methane	C−H	1.091	1.087
ethane	C−C	1.499	1.535
	C−H	1.093	1.094
	HCC	110.3	111.2
ethylene	C=C	1.319	1.339
	C−H	1.082	1.087
	CCH	122.3	121.3
acetylene	C≡C	1.206	1.202
	C−H	1.052	1.063
propene	C=C	1.321	1.336
	C−C	1.478	1.501
	C−H	1.082	1.081
	C−H	1.097	1.098
	CCC	123.4	124.3
	CCH	123.1	121.5
propyne	C≡C	1.207	1.206
	C−C	1.434	1.459
	C_1−H	1.053	1.056
	C_3−H	1.099	1.105
	CCH	111.2	110.2
allene	C=C	1.300	1.308
	C−H	1.087	1.087
	HCH	114.2	118.2
neopentane	C−C	1.504	1.539
	C−H	1.093	1.120
	HCC	110.1	110.0
cyclopropane	C−C	1.506	1.510
	C−H	1.076	1.074
	HCH	116.3	115.9
cyclopropene	C=C	1.302	1.296
	C−C	1.526	1.509
	HCC	153.1	149.9
	HCH	116.3	114.6
cyclopentadiene	C=C	1.339	1.345
	C−C	1.462	1.468
	C−C	1.498	1.506
benzene	C−C	1.385	1.397
	C−H	1.083	1.083
naphthalene	C_1−C_2	1.368	1.381
	C_2−C_3	1.403	1.417
	C_1−C_9	1.407	1.422
	C_9−C_{10}	1.419	1.412

[a] Bond lengths are in Å; bond angles are in deg.

Vibrations. In Table 9, we compare the calculated and experimental vibrational frequencies.[36] While vibrational frequencies were not employed as reference functions by the fitting of the parameters, vibrational spectra are well reproduced by PNTB. The calculated frequencies tend to be predicted somewhat too low. The C−H stretching frequencies are about 4% smaller than the observed values. The PNTB predictions for C−C, C=C, and C≡C bond-stretching modes in C_2H_6, C_2H_4, and C_2H_2 are calculated to be 1266, 1499, and 1895 cm^{-1}, respectively. These values agree within 10% with the experimental frequencies, 1388, 1623, and 1974 cm^{-1}. Even for torsional motion in C_2H_6, PNTB gives 206 cm^{-1}, in agreement with the experimental value 289 cm^{-1}. The lowest-energy bending mode Π_g in C_2H_2 is found to be

Table 9. Comparison of PNTB Vibrational Frequencies (in cm^{-1}) with Experimental Values (in Parentheses)

molecule	symmetry of vibration	PNTB (exptl)
hydrogen	Σ_g	4118 (4401)
methane	A_1	2928 (3158)
	T_2	2869 (3019); 1252 (1357)
	E	1397 (1534)
ethane	A_{1g}	2883 (2896); 1266 (1388); 975 (995)
	A_{2u}	2904 (2915); 1314 (1370)
	E_u	2840 (2974); 1373 (1460); 750 (822)
	E_g	2832 (2969); 1357 (1468): 1121 (1190)
	A_{1u}	206 (289)
ethylene	A_{1g}	2959 (3026); 1499 (1623); 1253 (1342)
	A_{1u}	916 (1023)
	B_{1u}	2978 (2990); 1315 (1444)
	B_{2g}	783 (943)
	B_{2u}	2954 (3106); 704 (810)
	B_{3g}	2939 (3103); 1080 (1236)
	B_{3u}	950 (949)
	A_{2u}	916 (1023)
acetylene	Σ_g	3245.9 (3374); 1895 (1974)
	Σ_u	3225.2 (3289)
	Π_u	826 (747)
	Π_g	355 (624)

355 cm^{-1}. This values agrees well with the 324 cm^{-1} from MP4/6311G* calculations.[36] The essential discrepancy with an experimental value, 624 cm^{-1}, appears to be mainly due to the anharmonicity of this mode.

Conclusions

We described a noniterative tight-binding model parametrized for calculating energetics and geometries of carbon and hydrocarbon systems. The scheme provides good estimates of the heats of formation and reaction enthalpies. The mean absolute error of the calculated ΔH_f is 4.6 kcal/mol, which is several times smaller than the errors found within related schemes. The method gives accurate estimates for C−H and C−C bond energies and isomerization reactions. This suggests the internal consistency of the predicted heats of formation, allowing a reliable analysis of trends across series of molecules. Molecular geometries of organic molecules are well predicted by PNTB; the mean absolute error of the bond lengths is 0.015 Å, and that of the bond angles is 1.4°. The calculated vibration frequencies reasonably agree well with experimental values. The method has proven to be transferable to complex carbon and hydrocarbon systems. Taking into account the computational efficiency and good performance of the model, we conclude that PNTB should be very promising for simulations of the formation of carbon nanostructures and the high-temperature degradation of hydrocarbons.

The PNTB results give impetus to the further development of parametrized tight-binding methods. We expect that the performance of the model can be improved (1) by adjusting the distance dependence of the resonance and overlap integrals and (2) by using more flexible short-range potentials (additional terms such as the pair-directed Gaussian functions [6] may be introduced to describe the dispersion interaction).

Supporting Information Available: Calculated and experimental heats of formation of 83 hydrocarbons (Table SI1); calculated and experimental geometries (Table SI2). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Thiel, W. *Adv. Chem. Phys.* **1996**, *93*, 703.

(2) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(3) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(4) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

(5) Thiel, W.; Voityuk, A. A. *J. Phys. Chem.* **1996**, *100*, 616.

(6) Repasky, M. P.; Chandrasekhar, J.; Jorgensen, W. L. *J. Comput. Chem.* **2002**, *23*, 1601.

(7) Giese, T. J.; Sherer, E. C.; Cramer, C. J.; York, D. M. *J. Chem. Theory Comput.* **2005**, *1*, 1275.

(8) Sattelmeyer, K. W.; Tubert-Brohman, I.; Jorgensen, W. L. *J. Chem. Theory Comput.* **2006**, *2*, 413.

(9) Ohno, K.; Esfarjani, K.; Kawazoe, Y. *Computational Material Science*; Springer: Berlin, 1999.

(10) Selvam, P.; Tsuboi, H.; Koyama, M.; Kubo, M.; Miyamoto, A. *Catal. Today* **2005**, *100*, 11.

(11) Slater, J. C.; Koster, G. F. *Phys. Rev. B* **1954**, *94*, 1498.

(12) Hoffman, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(13) Porezag, D.; Frauenheim, T.; Kohler, T.; Seifert, G.; Kaschner, R. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1995**, *51*, 12947.

(14) Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, J.; Haugk, M.; Frauenheim, T.; Suhai, S.; Seifert, G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *58*, 7260.

(15) Zheng, G. S.; Irle, S.; Elstner, M.; Morokuma, K. *J. Phys. Chem. A* **2004**, *108*, 3182.

(16) Kruger, T.; Elstner, M.; Schiffels, P.; Frauenheim, T. *J. Chem. Phys.* **2005**, *122*, 114110.

(17) Zheng, G. S.; Irle, S.; Morokuma, K. *Chem. Phys. Lett.* **2005**, *412*, 210.

(18) Omata, Y.; Yamagami, Y.; Tadano, K.; Miyake, T.; Saito, S. *Physica E* **2005**, *29*, 454.

(19) Xu, C. H.; Wang, C. Z.; Chan, C. T.; Ho, K. M. *J. Phys. Condens. Matter* **1992**, *4*, 6047.

(20) Wang, C. Z.; Chan, C. T.; Ho, K. M. *Phys. Rev. Lett.* **1991**, *66*, 189.

(21) Wang, Y.; Mak, C. H. *Chem. Phys. Lett.* **1995**, *235*, 37.

(22) Horsfield, A. P.; Godwin, P. D.; Pettifor, D. G.; Sutton, A. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 15773.

(23) Winn, M. D.; Rassinger, M.; Hafner, J. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1997**, *55*, 5364.

(24) Pan, B. C. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2001**, *64*, 155408.

(25) Zhao, J. J.; Lu, J. P. *Phys. Lett. A* **2003**, *319*, 523.

(26) Lu, J. P.; Wang, C. Z.; Ruedenberg, K.; Ho, K. M. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *72*, 205123.

(27) *NIST Chemistry WebBook*, NIST Standard Reference Database, No. 69; Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD. http://webbook.nist.gov (accessed Oct 2005).

(28) Epiotis, N. D.; Yates, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 461.

(29) Kundu, T.; Goodman, L.; Leszczinski, J. *J. Chem. Phys.* **1995**, *103*, 1523.

(30) Head-Gordon, M.; Pople, J. *J. Phys. Chem.* **1993**, *97*, 1147.

(31) Rubio, M.; Merchán, M.; Ortí, E. *Theor. Chim. Acta* **1995**, *91*, 17.

(32) Yu, J.; Sumathi, R.; Green, W. H. *J. Am. Chem. Soc.* **2004**, *126*, 12685.

(33) Kolesov, V. P.; Pimenova, S. M.; Pavlovich, V. K.; Tamm, N. B.; Kurskaya, A. A. *J. Chem. Thermodyn.* **1996**, *28*, 1121.

(34) Cioslowski, J.; Rao, N.; Moncrieff, D. *J. Am. Chem. Soc.* **2000**, *122*, 8265.

(35) Hedberg, K.; Hedberg, L.; Bühl, M.; Bethune, D. S.; Brown, C. A.; Johnson, R. D. *J. Am. Chem. Soc.* **1997**, *119*, 5314.

(36) *NIST Computational Chemistry Comparison and Benchmark Database*, NIST Standard Reference Database Number 101 Release 12; National Institute of Standards and Technology: Gaithersburg, MD, Aug 2005; Johnson, R. D., III, Ed. http://srdata.nist.gov/cccbdb (accessed Oct 2005).

CT600064M