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RE-EVALUATION OF 1,4-NON-BONDED INTERACTIONS IN MOLECULAR MECHANICS

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Analysis of the sum of two-centre terms obtained from semi-empirical molecular orbital calculations into atom-pair interactions revealed a unique behaviour of 1,4-non-bonded atom-pair interactions compared with 1,5- and longer range interactions. Explicit inclusion of a special 1,4-non-bonded interaction term in an MM2-like molecular mechanics scheme gave a test force field with good performance.

INTRODUCTION

Nearly 20 years ago, Wertz and Allinger[1] presented the '*gauche* hydrogen' hypothesis, according to which the *gauche*-1,4-H–H interaction plays a dominant role in determining the relative stability between conformers, e.g. axial and equatorial methylcyclohexane.[1] The conclusion was derived, however, on the basis of an early version of their molecular mechanics scheme containing a large and hard hydrogen atom. For this reason, the hypothesis was considered to be force field dependent,[2] and subsequently remained unattended until today.[3] In the course of our studies on the correspondence between the steric energy terms of molecular mechanics and the quantities obtained from molecular orbital (MO) calculations,[4] the unique role of 1,4-non-bonded interactions came to our notice. This paper describes the findings in some detail and reports the performance of a trial molecular mechanics force field which explicitly includes a special potential function for the 1,4-non-bonded interaction.

It has long been realized that the 1,4-interactions cannot be adequately represented by the conventional non-bonded interaction functions alone, hence the torsional potential function has been introduced to make up for the difference.[3] Nevertheless, we wish to ensure that this correction is sufficient, and that no other effect is missed in such a ubiquitous interaction as the 1,4-non-bonded type. In fact, the AMBER force field uses different van der Waals terms for 1,4- and for longer range interactions.[5]

Considering that the former is a two-centred phenomenon whereas the latter is more-than-two-centred, and that the semi-empirical molecular orbital (MO) methods generally use only one and two-centre integrals of electronic wavefunctions while neglecting the higher order integrals, we thought it possible to separate 1,4-non-bonded from torsional interactions. Our first task is to extract and dissect the two-centre energies from the total energy obtained from the semi-empirical MO calculation.

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PARTITIONING OF SEMI-EMPIRICAL MO ENERGIES

The idea of energy partitioning originates from Pople *et al.*,[6] and was applied to the interpretation of conformational energy by Gordon[7] and others.[8,9] In the semi-empirical MO method, the Fock matrix contains only one- and two-centred (e_{AB}) two-electron repulsion integrals in addition to one-electron integrals. The latter consists of a resonance integral (e_{res}, which arises from overlap between atomic orbitals of two separate atoms A and B), an exchange integral (e_{exc}, which comes from quantum mechanical part of electrostatic interaction) and a classical electrostatic term (e_{ele}):

$$e_{AB} = e_{res} + e_{exc} + e_{ele} \tag{1}$$

The sum of these terms over all non-bonded atom pairs in the molecule in question formally corresponds to the non-bonded interaction energy E_{nb} in molecular mechanics, which in turn is the sum of van der Waals (E_{vdw}) and electrostatic energies (E_{ele}):

$$\sum_{A<} \sum_{B} e_{AB} = E_{nb} = E_{vdw} + E_{ele} \tag{2}$$

The term e_{ele} in equation (1) involves electron–electron repulsion, nuclear–nuclear repulsion and electron–nuclear attraction, and should correspond to the electrostatic interaction term E_{ele} in molecular mechanics:

$$\sum_{A<} \sum_{B} e_{ele} = E_{ele} \tag{3}$$

Hence, the sum of the first two terms of equation (1), e_{res} and e_{exc}, should formally correspond to the van der Waals term in molecular mechanics not containing the torsional contribution

$$\sum_{A<} \sum_{B} (e_{ele} + e_{exc}) = E_{vdw} \tag{4}$$

Dissection of two-centre energies in semi-empirical MO calculations was performed by using an energy partitioning option (ENPART),[10] implemented in the MOPAC program package[11] after version 4. Small *n*-alkanes, from butane to hexane, were geometry optimized by using the AM1 Hamiltonian[12] in MOPAC and the dissected sum $\Sigma_{A<} \Sigma_{B} \int (e_{ele} + e_{exc})$ (henceforth abbreviated to $E_{res} + E_{exc}$) from these calculations was further partitioned into 1,4-, 1,5- and 1,6-types and also into H–H, H–C and C–C pairs, and plotted against atom–atom distances for all the molecules tested (Figures 1–3). It should be noted that such a simple correspondence between the MM and MO terms as mentioned above is possible only for semi-empirical MO energies and not for *ab initio* energies which contain contributions from multi-centred integrals. Henceforth, despite the well-known behaviour of the AM1 method, which sometimes gives unexpected

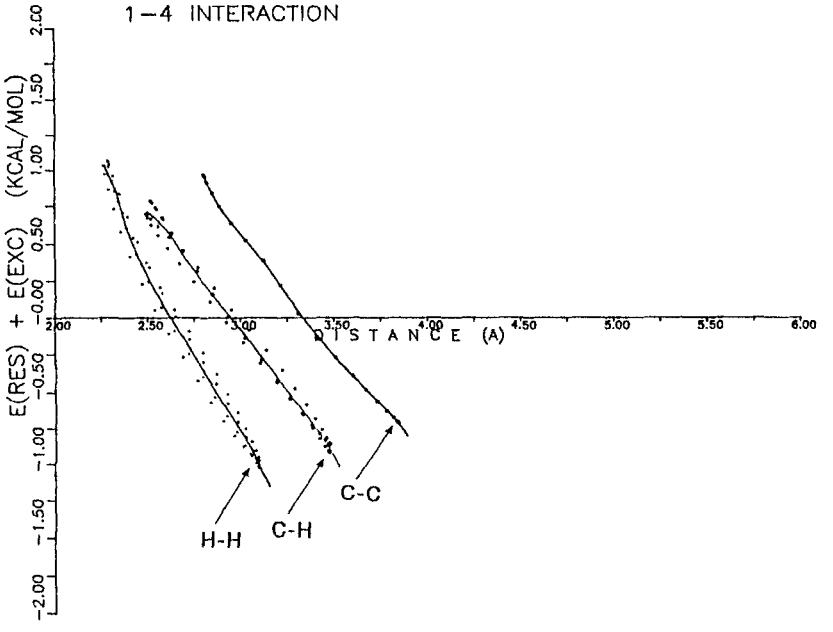

Figure 1. Dependence on distance of the sum of two-centre resonance and exchange terms obtained by the AM1 method for 1,4-H–H, -C–H and -C–C pairs in small alkanes

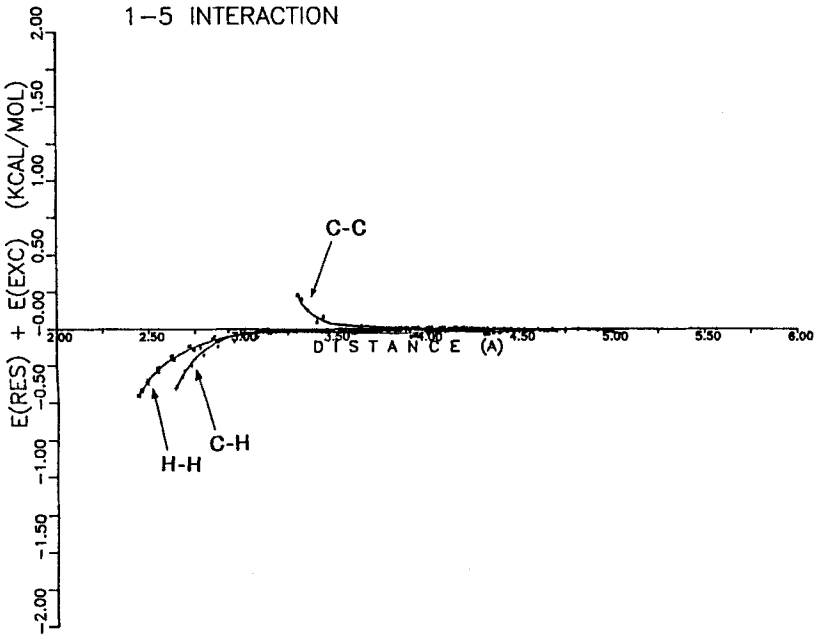

Figure 2. Dependence on distance of the sum of two-centre resonance and exchange terms obtained by the AM1 method for 1,5-H–H, -C–H and -C–C pairs in small alkanes

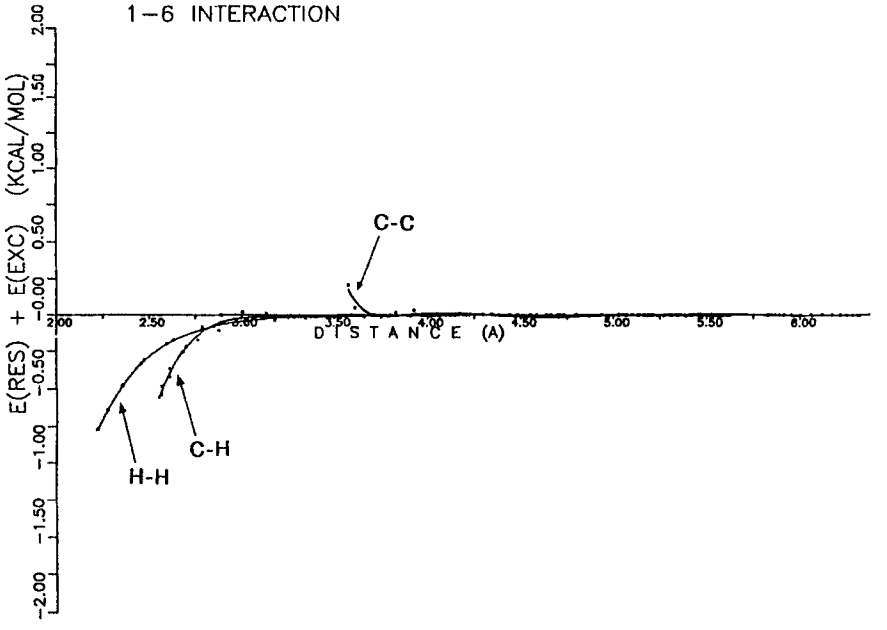

Figure 3. Dependence on distance of the sum of two-centre resonance and exchange terms obtained by the AM1 method for 1,6-H–H, -C–H and -C–C pairs in small alkanes.

results,[10,12] we cannot use *ab initio* method for our present purpose.

1,5- AND 1,6-PAIR INTERACTIONS

The energy *vs* distance curves of 1,5- and 1,6-C–C pairs indeed resemble the familiar van der Waals potential curve (Figures 2 and 3). However, the decrease in the $E_{res} + E_{exc}$ values of 1,5- and 1,6-H–C and H–H pairs with decrease in the interatomic distance is enigmatic. The reason for this behaviour is still unknown but is probably related to the strong anisotropy of orbitals involving hydrogen atoms. Except for these dips, the overall features of the 1,5- and 1,6-curves do not conflict with the isotropic van der Waals potential curve in that the energies are very small negative values at long distances and that there is even a small minimum in the region of the van der Waals diameters.

FEATURES OF 1,4-PAIR INTERACTIONS

The most remarkable aspect of Figures 1–3 is that the $E_{res} + E_{exc}$ sums for the 1,4-pairs (Figure 1) are totally different from those of longer interactions (Figures 2 and 3). The 1,4-C–C curve is repulsive when the distance is shorter than 3·3 Å and attractive when the distance is longer. For 1,4-C–H and H–H pairs, the threshold values are 2·9 and 2·6 Å, respectively. Note that these three threshold values coincide perfectly with those distances at which the MM2 van der Waals curves for C–C, C–H and H–H interactions change the sign in the repulsive region.[3]

Although the $E_{res} + E_{exc}$ curves for 1,4-pairs may appear to be a part of longer curves, the distance values that can be taken between the 1,4-pair atoms are limited, and actually oscillate along these curves as the central bond between the 1,4-pair rotates. The relationship is better illustrated by Figure 4, where $E_{res} + E_{exc}$ values are plotted against dihedral angle of the four-atom system. This 'cosine' curve has a maximum at *syn* and a minimum at *anti* conformations, and vanishes at a perpendicular orientation of the two vicinal bonds in the four-atom system.

How can we interpret the 1,4-pair interaction curve as given in Figure 1? Neither hyperconjugation nor through-bond orbital interaction is likely to be the reason for the special behaviour of 1,4-non-bonded interactions, because the former would have given a twofold cosine curve[13] while the latter is not dependent on the bond rotation.[14] Despite all the risks from the approximations used in the semi-empirical MO method, it is tempting to attribute the strong repulsion in the *syn* conformation to the repulsive van der Waals-type interaction across the short space, and the strong attraction in the *anti*-periplanar form to a non-bonded interaction unique to the 1,4-type, which in this case acts entirely by way of nuclei and bonding electrons.

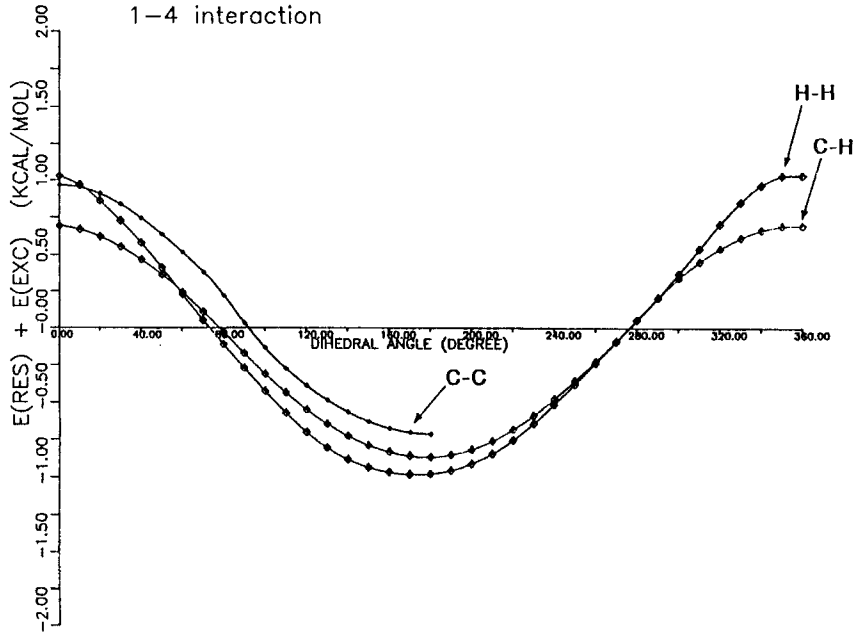

Figure 4. Dependence on the rotation about the central bond of the sum of two-centre resonance and exchange terms for 1,4-H–H, -H–C and -C–C pairs in small alkanes

An interesting trend was reported in a carbon-13 chemical shift study[15] which clearly supports our interpretation mentioned above. It is observed that two vicinal hydrogens in an *anti* relationship contribute to a downfield shift for each of the carbon atoms involved (H—C—C—H). On the other hand, the same hydrogen pair in a *gauche* disposition (hence congested and in repulsive interaction) causes a strong upfield shift of the carbon atoms.[15]

CONSTRUCTION OF A TEST FORCE FIELD EXPLICITLY CONTAINING SPECIAL 1,4-NON-BONDED VAN DER WAALS POTENTIAL

From a practical point of view, it appears interesting to implement into the molecular mechanics force field a new potential function that reproduces the 1,4-interaction curves in Figure 1 and to see how the performance of a force field is affected by such a change. The remainder of this paper describes the results of an attempt in this direction. The purpose of this section is not to compare the practical usefulness of the test force fields and MM2, hence only the structures and vibrational frequencies are compared and no attempt was made to compare energies.

We used MM2[3] as the starting, basis force field and systematically changed it in the course of this study. In order to assess the effect of a new potential function, parameters of potential functions were optimized using a non-linear least-squares optimization program (SOPE, Selection and Optimization of Potential Energy Functions and Parameters for Molecular Mechanics),[16] which was originally taken from Rasmussen's version of Consistent Force Field[17] and developed into an independent and flexible program. In the present version, SOPE contains most of the potential functions used in MM2 and CFF.[18]

Standard set

For the structure, only the gas-phase electron diffraction data were used for consistency. Ethane, propane, *n*-butane, isobutane, cyclopentane, neopentane and cyclohexane, were chosen as the standard molecules for the test force field (Table 1).[19] It was planned from the beginning to implement into the test force field the capability of calculating vibrational frequencies.[20,21] Vibrational frequencies of the standard hydrocarbons in the infrared region were taken from the work of Schachtschneider and Snyder[22] and those in the far-infrared region from recent inelastic neutron scattering studies.[23]

Potential functions

Unless indicated otherwise (see below), potential energy functions of MM2 were utilized as far as possible. The only exception is the stretching potential, E_s, which was replaced with a Morse function:

$$E_s = A_{exp}[-B(r-C)]\{\exp[-B(r-C)-2\cdot0]\} \quad (5)$$

where A, B and C are adjustable parameters and r and C correspond to the actual and 'natural' interatomic distances, respectively. The Morse function is known to dramatically improve the performance of molecular mechanics in vibrational calculations.[24] The same potential was also used for describing the new 1,4-non-bonded van der Waals potential, partly because Stølevik and co-workers[25] have long recommended the use of this function for non-bonded interactions.

Table 1. Experimental and calculated structures of small hydrocarbons

Compound	Parameter[a]	Exptl[b]	FF2[c]	MM2[d]
Ethane	r(CC)	1·534	1·536	1·532
	r(CH)	1·112	1·113	1·115
	θ(CCH)	111·0	110·4	111·0
Propane	r(CC)	1·532	1·537	1·534
	r(CH)	1·107	1·113	1·115
	θ(CCC)	112·0	111·8	111·7
Isobutane	r(CC)	1·535	1·541	1·537
	r(CH)	1·113	1·113	1·114
	θ(CCC)	110·8	110·2	110·6
n-Butane	r(CC)	1·531	1·540	1·535
	r(CH)	1·117	1·113	1·115
	θ(CCC)	113·8	111·7	11·8
Cyclopentane	r(CC)	1·546	1·540	1·540
Neopentane	r(CC)	1·534	1·543	1·541
	r(CH)	1·114	1·114	1·114
	θ(CCH)	112·0	110·6	111·3
Cyclohexane	r(CC)	1·536	1·541	1·536
	r(CH)	1·121	1·114	1·116
	θ(CCC)	111·4	111·1	110·9

[a] Bond distances (r) in Å and valence angles (θ) in degrees.
[b] Ref. 19.
[c] This work.
[d] Ref. 3.

Evaluation of test force fields

The performance of force field was judged in terms of the root-mean-square, rms_w of the errors in the calculation of molecular geometries and vibrational frequencies as compared with the experimental values of the standard molecules, weighted with inverse uncertainties in the experimental measurements:

$$rms_w = \sqrt{[\Sigma\ (\text{error/uncertainty})^2]/n} \quad (6)$$

where n is the number of data points. Uncertainties in the vibrational frequencies are not reported in the literature,[22] but were assumed to be 30 cm^{-1}. The

Table 2. Weighted root-mean-square errors [rms_w, equation (6)] of MM2, and trial force fields, FF1 and FF2, in the calculation of molecular structures and vibrational frequencies

Force field	Standards	
	Geom.[a]	Geom. + vib.[b]
MM2	23·5	80·6
FF1[c]	38·9	45·2
FF1 without SB[d]	32·0	39·4
FF2[e]	24·8	36·0

[a] Experimental structures (Table 1) are used as the standards of the parameter optimization process.
[b] Both experimental structures and vibrational frequencies are used as the standards.
[c] Stretching potential function of MM2 was replaced with Morse function.
[d] Stretch–bend cross-term was removed from FF1.
[e] 1,4-van der Waals potential function was added to FF1.

program SOPE calculates rms_w before and after the optimization of the parameters set.

We first attempted to re-optimize the original MM2 parameters using only the experimental geometries of our small standard hydrocarbon set, but our SOPE program did not produce any change in the MM2 parameters. This test confirmed that the current MM2 parameters are well optimized for the simple set of hydrocarbons used here. The rms_w value for this original MM2 hydrocarbon parameters set is calculated to be 23·5 (Table 2). When vibrational frequency data were included in the standard and parameters were re-optimized, the rms_w value increased to 80·6. This is understandable since MM2 has never been parameterized to reproduce vibrational spectra.[26]

FF1

The first trial force field (FF1) included the special 1,4-non-bonded potential but was prepared by replacing the quadratic stretching potential (augmented with a sixth-power correction term) of MM2 with a Morse function [equation (5)]. When only the three new parameters in the Morse function were optimized with SOPE against our standard structural and vibrational data, the rms_w value decreased from 80·6 to 62·3. The improvements in rms_w must have come from the better fit of the Morse potential to the experimental vibrations.

When bending parameters (C—C—C, C—C—H and

Table 3. Final parameters of FF2 trial force field[a]

	Morse parameters		
	A (kcal mol^{-1})[b]	B (Å^{-1})	C (Å)
Stretch (r = 1 Å):			
C—C	105·0	1·80	1·113
C—H	86·0	2·03	1·536
1,4-van der Waals (r = interatomic distance):			
C···C	14·524	0·4685	18·056
C···H	2·031	0·7447	10·592
H···H	0·284	1·1837	4·692
	Bending parameters		
	k_θ (mdyn Å^{-1} rad^{-1})[c]	θ_0(°)	Type[d]
C—C—C	—	109·71	2
	—	109·75	3
C—C—H	0·62	110·77	3
H—C—H	0·51	—	—

[a] Only the new parameters and those which changed during the optimization process are entered here. Otherwise, the original MM2 parameters are used without change. A, B and C are the parameters of Morse function [equation (5)]. Parameters k_θ and θ_0 are defined in the MM2 bending potential function. $E_b = 0{\cdot}021914 k_\theta (\theta - \theta_0)^2\{1 + 7 \times 10^{-8}(\theta - \theta_0)^4\}$.
[b] 1 kcal = 4·194 kJ.
[c] 1 mdyn = 10^{-8} N.
[d] Central carbon of type 2 angle carries one hydrogen atom (—CRH—) and type 3 angle two hydrogen atoms (—CH_2—).

Table 4. Performance of FF2 force field in vibrational calculation for small hydrocarbons[a]

Compound	N[b]	Max. Obs.	Max. Calc.	Min. Obs.	Min. Calc.	Error[c] Av.[d]	Error[c] SD[e]
Ethane	13	2974	2982	303	263	0·7	37·3
Propane	24	2965	2983	236	193	15·2	56·8
n-Butane	31	2965	2982	167	101	12·2	55·3
Isobutane	23	2965	2976	234	195	22·0	53·2
Neopentane	12	2953	2972	335	236	22·6	52·0
Cyclohexane	28	2939	2978	250	179	8·8	65·6
Total	131					13·5	56·2

[a] Experimental frequencies are taken from Refs 22 and 23. Frequencies are given in cm^{-1}.
[b] Number of observed absorption bands.
[c] Obs. – calc. (FF2).
[d] Averaged absolute error.
[e] Standard deviation.

H—C—H) were included as the targets of optimization, in addition to the Morse parameters, a still better rms_w value of 45·2 was obtained (Table 2). At this stage, re-optimization without vibrational frequencies resulted in a considerably improved rms_w value of 38·9 (Table 2).

Further attempts to re-optimize other parameters did not bring any significant change, but one observation may be worth noting. Removal of the stretch–bend cross-term and re-optimization of all the parameters with SOPE gave slightly improved rms_w values of 39·4 (geometry + vibration) and 32·0 (geometry only) (Table 2). These are the best results for the FF1 force field, but we stopped working with FF1 at this point since our tentative goal of reducing rms_w to near 24 of MM2 itself does not appear to be possible with FF1.

FF2

Based on the analysis of the two-centre terms in semi-empirical MO results as mentioned above, the van der Waals part of FF1 was changed so that it calculates only 1,5- and longer-range non-bonded pairs of atoms, and a new Morse potential was introduced to take care of 1,4-non-bonded interactions. All of the parameters used in FF1 were re-optimized, together with the new Morse parameters. Whereas none of the long-range van der Waals and torsional parameters was affected during optimization, many bending parameters changed. The final, changed and new parameters of FF2 are summarized in Table 3. Note that the values of the constant C in the new 1,4-non-bonded potential function given in Table 3 are too large for van der Waals radii of the atoms concerned. We believe that this correspondence[25] is not appropriate here, possibly owing to the large anisotropy in the forces acting between the 1,4-atom pair.

The new rms_w value for geometry obtained was low, 24·8, almost the same level as in the original MM2. Inclusion of vibrational frequencies as the standard led to a new low rms_w value of 36·0 (Table 2). Structural features resulting from FF2 and MM2 calculations are compared with experimental standards in Table 1. Table 4 summarizes the results of the vibrational calculations for the standard hydrocarbons. The overall standard deviation in errors for 131 data points was 56 cm^{-1}, which can be considered fairly good for an unscaled comparison.[26]

DISCUSSION

Inclusion of a new 1,4-non-bonded interaction potential without changing the torsional potential function and parameters of MM2 might appear to cause some redundancy in the one-fold term of the latter. The one-fold cosine shape of 1,4-interaction as given in Figure 4 reminds us of its possible connection with the one-fold component of the torsional potential widely used in molecular mechanics:[3]

$$E_\omega = \frac{V_1}{2}(1 + \cos\omega) + \frac{V_2}{2}(1 - \cos 2\omega) + \frac{V_3}{2}(1 + \cos 3\omega) \quad (7)$$

The V_1 term, is proposed to arise from the bond dipole–bond dipole interaction.[27]

In spite of the vertical shift between these two curves [Figure 4 and the V_1 term in equation (7)] mentioned above, both will have the same effect in the geometry optimization and in the comparison of potential energies. The risk is considered minimal, however, for the following reasons. First the V_1 parameters of equation (7) for H—C—C—H and H—C—C—C are actually

zero in MM2.[3] Second, re-optimization of parameters with SOPE affected none of the torsional constants for the C—C—C—C unit. Hence the 1,4-van der Waals potential of FF2 and the torsional potential of MM2 do not correlate with each other.

A more critical question regarding the present results is why FF2 did not give a better rms_w value for geometry than MM2. A likely answer is that the molecular mechanics scheme has so much flexibility that it can absorb some defects, in either FF2 or MM2, by adjusting parameters. In fact, it is not safe to make a comparison only in terms of the structural performance since the number of structural data used here is not large enough compared with the number of parameters.

In this particular case, it is more reasonable to compare the 'hypothetical behaviour' of MM2 for geometry + vibration with FF2. In this comparison, the new 1,4-non-bonded potential does show a positive effect. Even though the remarkable effect of replacing the quadratic stretch potential with a Morse function appears to overwhelm the relative importance of the 1,4-interaction term, we propose to pay more attention to the 1,4-non-bonded interaction, not only with regard to H–H but also to H–C, C–C pairs and perhaps other combinations. The 1,4-interaction is intermediate in nature between the bonded and non-bonded interactions, hence it reasonably needs a special potential function.

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