Density functional study of polypropylene and its submolecules

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Previous density functional (DF) calculations of the structures of small hydrocarbon molecules (CH, CH_2, C_2H_2, C_2H_4, C_3H_6, C_3H_8) have been extended to larger systems. The structure of a single chain of isotactic polypropylene (*it*-PP) has been optimized, and calculations have been performed for smaller molecules with closely related structures (propane C_3H_8, several conformers of isopentane C_5H_{12}, and 2,4,6-trimethyl heptane $C_{10}H_{22}$) using both local spin density (LSD) and non-local (gradient-corrected) energy functionals. The pronounced transferability of the local structural parameters between C_5H_{12}, $C_{10}H_{22}$ and *it*-PP suggests that the energy surfaces calculated for molecules with five carbon atoms should provide a very good representation of the local energy variations in much larger systems. © *1997 American Institute of Physics.*
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I. INTRODUCTION

The density functional (DF) formalism[1] is widely used for calculating structural and cohesive properties of bulk systems, and the extension to small molecules and clusters over the past 15 years or so has shown that it can also provide a reliable and economical approach in these cases. The coupling of DF calculations with molecular dynamics (MD)[2] allows the total energy to be found for a range of geometrical configurations inaccessible to many other methods, and the use of non-local modifications of the parameter-free local spin density (LSD) approximation for the exchange-correlation energy has improved the agreement with measured formation energies.

Organic polymers are of great technological importance and have been the subjects of numerous DF studies,[3] examples being single chains of *trans*-polyacetylene[4] and polyethylene.[5] The application of combined MD/DF calculations to organic molecules is complicated by their use of a pseudopotential description of the electron-ion interaction and a plane-wave basis, since the rapid variations of the pseudopotentials of first-row atoms (such as C, H, O) requires very large plane-wave expansions. While the combination of MD with DF or correlated wave function schemes using Gaussian basis functions is a promising alternative,[6] the applicability of the MD/DF scheme has been enhanced by the development of ''soft'' pseudopotentials.[7] We showed recently that such calculations could be used to study structures and energy differences in small hydrocarbon molecules (CH, CH_2, C_2H_2, C_2H_4, C_3H_6, C_3H_8).[8] For both LSD and non-local (gradient-corrected) approximations, the structures and energy barriers, including those for rotation about single and double bonds, generally agree well with available experimental findings and the results of wave function-based calculations, and with the results of all-electron DF calculations using a Gaussian basis. Recent studies of some organic reactions also give an encouraging view of the application of DF theory,[9] although current approximations to the exchange-correlation energy often underestimate the energy barriers.

A major goal of this work is to study the extent to which the structural properties of small molecules can be used to predict the energy surfaces of composite systems, i.e., those containing the smaller molecules as structural units. A similar study using the Hartree-Fock approximation was carried out some years ago for some small straight-chain[10] and branched[11] hydrocarbons, with particular focus on the conformational behavior (the dependence of the dihedral angles along the carbon chains). Here we extend the DF study mentioned above to larger molecules.

In the present paper we present the results of calculations on several conformers of isopentane (C_5H_{12}), and we then describe calculations (with both LSD and gradient-corrected approximations to the exchange-correlation energy functional) of the structure of a single chain of isotactic polypropylene (*it*-PP). With three C_3H_6 units (27 atoms) in the unit cell, this is one of the largest polymer chains for which the structure has been optimized fully in a DF calculation. We have also performed DF calculations on the structures and energy differences in molecules (propane C_3H_8, and 2,4,6-trimethyl heptane, $C_{10}H_{22}$), which, together with isopentane, have structures that may be viewed as submolecules of the *it*-PP chain. We have performed both MD/DF and all-electron calculations on propane and isopentane, and again find very good agreement between the two sets of calculations. For $C_{10}H_{22}$ we have carried out all-electron calculations with the distance between two extremal C atoms constrained to equal the experimental value of the corresponding distance in *it*-PP. Possible extensions of this study include the parametrization of the classical force fields in larger systems or developing ''coarse-grained'' models that would allow much larger systems to be investigated efficiently using methods such as classical MD.

In Sec. II we provide essential details of the calculations, and in Sec. III present results for the structures of the above systems. The results are compared with experimental and theoretical work where available. We discuss our findings and give our conclusions in Sec. IV.

II. METHODS OF CALCULATION

Details of the numerical methods used in the calculations of small molecules have been given previously.[8,12] The present MD/DF calculations were performed with periodic boundary conditions and simple cubic unit cells. The lattice constants [18 a.u. in C_3H_8, 21 a.u. in C_5H_{12}] are large enough to ensure that there is negligible interaction between neighboring molecules. As in the earlier study of smaller organic molecules,[8] the pseudopotential for C and H used to describe the electron-ion interaction had the (non-local) form suggested by Troullier and Martins.[7] The basis set expansion was taken to be plane waves, with an energy cutoff of 30 a.u., and we use a single point ($\mathbf{k}=0$) in the Brillouin zone.

The density functional calculations on the single chain of *it*-PP were also performed using periodic boundary conditions in three dimensions. The unit cell was chosen to be simple tetragonal, with lattice constants in the directions perpendicular to the chain that were again large enough (20.75 a.u.) to ensure a minimal interchain interaction. The lattice parameter in the direction of the chain axis was initially set equal to the experimental value (12.26 a.u., 6.50 Å).[13] The optimum structure was determined by calculating the forces on the atoms, which were then allowed to relax to the structure with minimum energy. The calculation was repeated with different lattice parameters along the direction of the chain, in order to optimize *all* structural parameters for the single *it*-PP chain. The electron-ion interaction for C and H was described by the same pseudopotential[7] as in the work on isolated molecules, and the plane wave basis had the same energy cutoff (30 a.u.). The integration in reciprocal space employed the special points technique,[14] and a thorough check showed that both the cutoff of 30 a.u. and eight special points gave well-converged results. The numerical accuracy of the interatomic separations, for example, should be better than 0.01 Å.

The choice of energy functional is an important consideration in DF calculations. In addition to the local spin density (LSD) approximation, which is based on accurate calculations of the exchange-correlation energy density in a homogeneous, spin-polarized electron gas, we have used a non-local, gradient-corrected functional with the exchange part due to Becke[15] and the correlation part due to Perdew[16] (the ''BP'' functional). For isopentane and $C_{10}H_{22}$ we have also performed all-electron DF calculations with a Gaussian basis set[17] using the same two functionals. These calculations provide independent checks of the use in our MD/DF calculations of both the pseudopotential approximation and the plane-wave basis set.

III. RESULTS

The structures of the molecules considered here are shown in Fig. 1, which shows the transition from propane [C_3H_8, Fig. 1(a)] to the most stable forms of isopentane [C_5H_{12}, Fig. 1(b)], $C_{10}H_{22}$ [Fig. 1(c)] and *it*-PP [Fig. 1(d)]. The hydrogen atoms are shown grey, and the relationship between the positions of the carbon atoms is shown by marking black those that are the same as in the smaller system and marking white those that are new. Figure 1(d) shows more than a single unit of the *it*-PP chain, in order to make the comparison clearer.

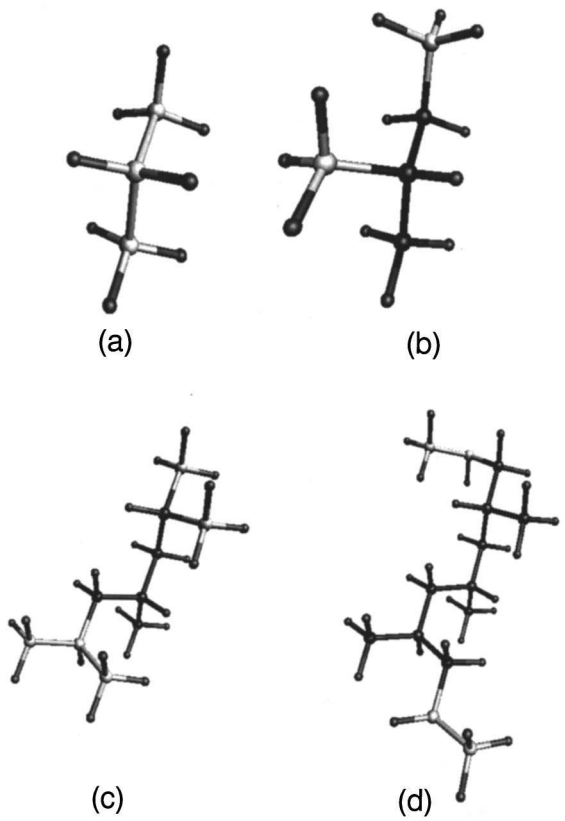

FIG. 1. Structures of (a) propane, (b) isopentane, (c) $C_{10}H_{22}$, and (d) isotactic polypropylene. Black carbon atoms indicate the structure of the previous molecule in the series.

A. Isopentane

Isopentane (IP) has a variety of conformers, and we have performed MD/DF calculations on those shown in Fig. 2. Conformer IP(2) is obtained form IP(1) by rotating the $C(CH_3)(CH_3)(H)$ group by 60° with respect to the $C(CH_3)(H)(H)$ group; IP(3) is obtained from IP(2) and IP(4) from IP(3) by rotating the same group in the same way by 120° and 60°, respectively. The conformer denoted (3, rotated methyl) is related to IP(3) by rotating the methyl group on C(5) by 60°, and it is less stable than IP(3) by 3.07 kcal mol^{-1}. As shown in Table I, there is satisfactory agreement between the optimized structures obtained here with the LSD approximation and those obtained with Hartree-Fock (HF) calculations.[11,18] Our DF calculations lead to C–H bonds that are slightly longer than the HF values, which is consistent with earlier findings[19] that the LSD approximation tends to overestimate the lengths of bonds between H and main group elements.

The most stable structure of isopentane is found to be (3), which occurs indeed as a structural unit in both $C_{10}H_{22}$ and *it*-PP. Conformer (2) lies 0.83 kcal mol^{-1} higher, followed by (4) (3.41 kcal mol^{-1} above the ground state) and (1) (5.19 kcal mol^{-1}). The ordering is the same as that found

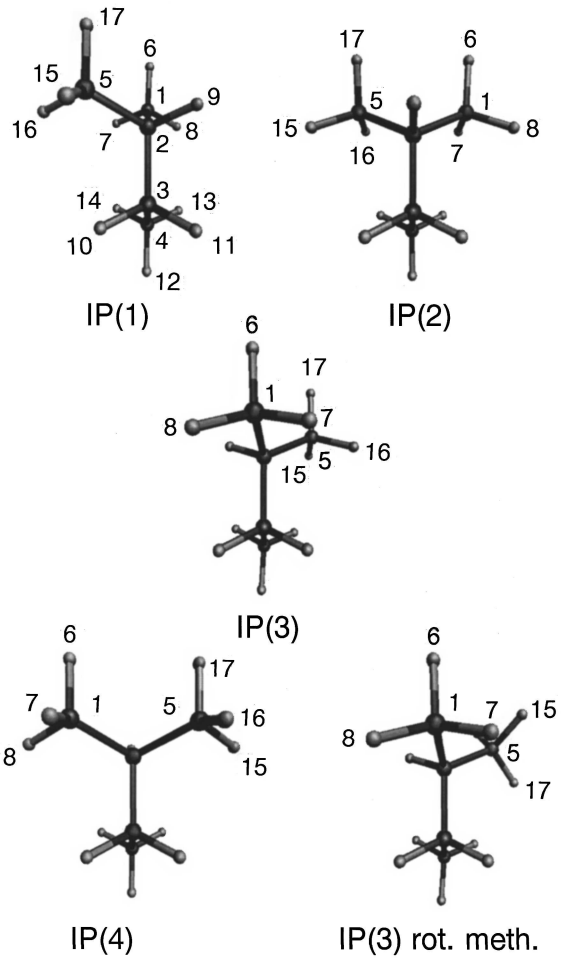

FIG. 2. Optimized MD/DF structures of five conformers of isopentane (IP, C_5H_{12}).

TABLE I. Optimized bond distances and angles for conformers (1–4) of isopentane (bond lengths d in Å, bond angles α in degrees). The relative energies ΔE are given in kcal mol^{-1}.

Param	(1) [a]	(2) [a,b]	(3) [a,b]	(4) [a,b]
ΔE	5.6, 5.19	0.9, 0.83	0.0, 0.0	3.0, 3.41
$d_{C_2C_1}$	1.544, 1.515	1.543, 1.519	1.543, 1.518	1.542, 1.519
$d_{H_6C_1}$	1.084, 1.107	1.084, 1.108	1.084, 1.109	1.084, 1.109
$d_{H_7C_1}$	1.083, 1.109	1.083, 1.110	1.085, 1.109	1.084, 1.108
$d_{H_8C_1}$	1.082, 1.107	1.084, 1.108	1.084, 1.108	1.084, 1.109
$d_{C_3C_2}$	1.572, 1.552	1.550, 1.532	1.547, 1.526	1.562, 1.542
$d_{C_5C_2}$	1.544, 1.517	1.542, 1.519	1.542, 1.518	1.542, 1.519
$d_{H_9C_2}$	1.084, 1.113	1.086, 1.116	1.086, 1.118	1.085, 1.117
$d_{C_4C_3}$	1.543, 1.514	1.542, 1.516	1.542, 1.516	1.542, 1.516
$d_{H_{10}C_3}$	1.084, 1.112	1.085, 1.112	1.085, 1.112	1.084, 1.112
$d_{H_{11}C_3}$	1.084, 1.109	1.085, 1.113	1.086, 1.114	1.084, 1.112
$d_{H_{12}C_4}$	1.084, 1.106	1.084, 1.107	1.084, 1.108	1.084, 1.109
$d_{H_{13}C_4}$	1.082, 1.107	1.082, 1.108	1.082, 1.109	1.084, 1.108
$d_{H_{14}C_4}$	1.082, 1.107	1.082, 1.108	1.084, 1.108	1.084, 1.108
$d_{H_{15}C_5}$	1.084, 1.107	1.084, 1.108	1.082, 1.109	1.084, 1.108
$d_{H_{16}C_5}$	1.085, 1.110	1.083, 1.110	1.085, 1.109	1.084, 1.109
$d_{H_{17}C_5}$	1.084, 1.108	1.084, 1.108	1.084, 1.108	1.084, 1.109
$\alpha_{H_6C_1C_2}$	109.6, 110.4	110.4, 111.3	110.9, 111.6	110.9, 111.9
$\alpha_{H_7C_1C_2}$	111.2, 111.6	111.1, 111.2	110.3, 110.4	110.4, 110.6
$\alpha_{H_7C_1H_6}$	107.9, 107.2	107.8, 107.1	108.1, 107.3	108.2, 107.4
$\alpha_{H_8C_1C_2}$	111.7, 112.5	110.9, 111.7	111.0, 111.8	110.8, 111.6
$\alpha_{H_8C_1H_6}$	107.9, 107.6	108.2, 107.8	108.3, 107.9	108.2, 107.8
$\alpha_{H_8C_1H_7}$	108.4, 107.4	108.3, 107.6	108.2, 107.5	108.2, 107.4
$\alpha_{C_3C_2C_1}$	114.8, 114.6	112.2, 112.4	110.0, 110.8	111.4, 112.0
$\alpha_{C_5C_2C_1}$	109.7, 110.0	110.7, 111.0	110.0, 110.4	110.5, 110.7
$\alpha_{C_5C_2C_3}$	110.3, 110.8	112.2, 112.4	112.1, 112.3	111.3, 112.0
$\alpha_{H_9C_2C_1}$	106.9, 106.7	107.5, 107.3	108.2, 108.1	107.6, 107.5
$\alpha_{H_9C_2C_3}$	107.5, 107.3	106.4, 106.1	108.0, 107.1	108.1, 106.8
$\alpha_{H_9C_2C_5}$	107.4, 107.1	107.5, 107.3	108.4, 108.0	107.7, 107.5
$\alpha_{C_4C_3C_2}$	116.8, 117.5	115.4, 115.8	114.2, 115.3	112.7, 114.1
$\alpha_{H_{10}C_3C_2}$	108.5, 107.9	108.4, 108.3	108.4, 108.2	109.7, 109.2
$\alpha_{H_{10}C_3C_4}$	107.8, 108.4	108.8, 109.1	108.7, 109.3	108.9, 109.3
$\alpha_{H_{11}C_3C_2}$	108.7, 108.9	108.4, 108.3	108.8, 108.1	109.7, 109.2
$\alpha_{H_{11}C_3C_4}$	108.3, 108.5	108.8, 109.1	109.6, 109.9	109.1, 109.4
$\alpha_{H_{11}C_3H_{10}}$	106.2, 104.8	106.8, 105.7	106.9, 105.5	106.5, 105.4
$\alpha_{H_{12}C_4C_3}$	109.6, 110.7	110.0, 111.2	110.5, 111.7	111.1, 112.4
$\alpha_{H_{13}C_4C_3}$	111.6, 112.3	111.4, 111.8	111.6, 111.9	110.6, 111.2
$\alpha_{H_{13}C_4H_{12}}$	107.8, 107.2	107.8, 107.2	107.8, 107.2	108.2, 107.4
$\alpha_{H_{14}C_4C_3}$	111.5, 112.1	111.4, 111.8	110.6, 111.1	110.6, 111.1
$\alpha_{H_{14}C_4H_{12}}$	107.8, 107.2	107.8, 107.2	108.0, 107.3	108.2, 107.4
$\alpha_{H_{14}C_4H_{13}}$	108.3, 107.1	108.3, 107.4	108.2, 107.3	108.1, 107.1
$\alpha_{H_{15}C_5C_2}$	110.9, 111.7	110.9, 111.7	111.7, 112.4	110.8, 111.6
$\alpha_{H_{16}C_5C_2}$	110.3, 110.4	111.1, 111.2	110.2, 110.3	110.4, 110.6
$\alpha_{H_{16}C_5H_{15}}$	108.2, 107.4	108.3, 107.6	108.3, 107.6	108.2, 107.4
$\alpha_{H_{17}C_5C_2}$	110.9, 111.8	110.4, 111.3	110.4, 111.3	111.0, 111.9
$\alpha_{H_{17}C_5H_{15}}$	108.2, 107.9	108.2, 107.8	107.9, 107.6	108.2, 107.7
$\alpha_{H_{17}C_5H_{16}}$	108.2, 107.5	107.8, 107.1	108.1, 107.4	108.2, 107.4

[a]Hartree-Fock calculations [Ref. 11].
[b]Present work.

in HF calculations,[11] and the relative energies (the HF values are 0.9, 3.0, 5.6 kcal mol^{-1}) are in reasonable agreement. Figure 3 shows Newman plots of structures (1–4) viewed down the axis from C(4) to C(3) (see Fig. 4 for the labeling of atoms) and makes plausible the relative stability of IP(3). IP(1) has two eclipsed CH_3 groups on opposite sides of the molecule, and these steric interactions result in the highest energy. IP(4) also has an eclipsed form, but each methyl group eclipses a single hydrogen atom. While both IP(2) and IP(3) are staggered, the former has a higher energy since the two front methyl groups are *gauche* to the back CH_3 group, while one of the front methyl groups in IP(3) is *gauche* and the other *trans*. The bond lengths and angles and the dihedral angles given in Table II for these four structures provide more information about these steric effects.

The results of a vibrational analysis of the most stable conformer (3) using all-electron calculations[17] are shown in Table III, together with experimental results[20,21] and other calculations.[20,22] Vibration frequencies above 2000 cm^{-1} correspond to C–H stretching, the 1400–1500 cm^{-1} range to H–C–H bending, and frequencies from 300–1400 cm^{-1} to wagging, bending, rocking, and twisting. Frequencies below 300 cm^{-1} arise from torsional motions. The overall agreement with the earlier work is satisfactory. Table IV shows that the structural parameters calculated using the MD/DF method (pseudopotential description of the electron-ion interaction, plane-wave basis set) and all-electron DF calculations (Gaussian basis set) are in excellent agreement.

B. Isotactic polypropylene

Isotactic polypropylene occurs in three different crystalline structures: a monoclinic α-form, first reported by Natta

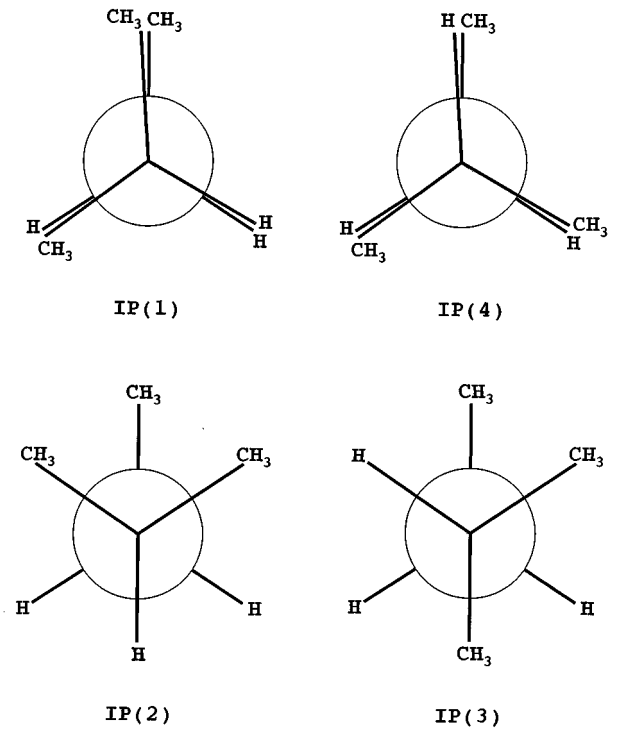

FIG. 3. Structures of conformers (1–4) of C_5H_{12} shown as Newman projections, viewed down the axis from C(4) to C(3).

and Corradini,[13] a hexagonal β-form and a triclinic γ-form. In spite of the structural differences, there is considerable experimental evidence[13,23,24] that these forms comprise just two enantiomorphic chain conformations: right-handed and left-handed (3/1) helices, with a periodicity of 6.5 Å. This suggests that intramolecular forces play a central role in the conformation of the chains in the crystalline structure. The helix is such that the backbone dihedral angles alternate between *trans* and *gauche*. Although the *gauche* torsions have

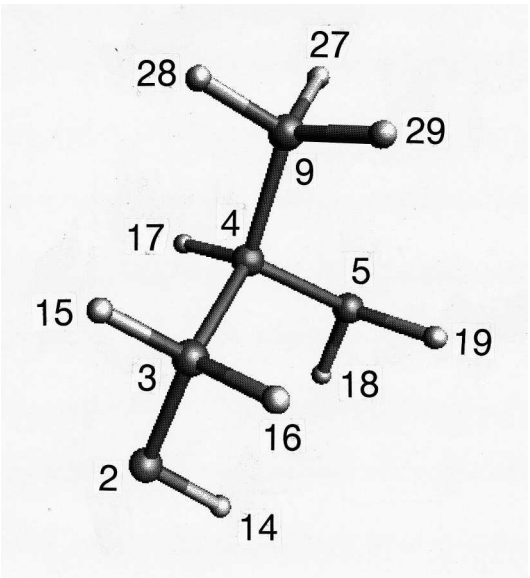

FIG. 4. Section of C_5H_{12} with labeling of atoms used in Table IV.

TABLE II. Comparison of bond lengths d_{CC}, bond angles α_{CCC} and dihedral angles γ_{CCCC} for conformers of C_5H_{12} (bond lengths in Å, angles in degrees). Figure 4 shows the atom labels.

Conformer	γ_{2349}[a,b]	α_{234}[a,b]	d_{34}[a,b]
(1)	0, −0.2	116.8, 117.5	1.572, 1.552
(4)	120, 119.4	112.7, 114.1	1.562, 1.542
(2)	−62.7, −63.0	115.4, 115.8	1.550, 1.532
(3)	173.8, 173.4	114.2, 115.3	1.547, 1.526

[a]Hartree-Fock calculations, Ref. 11.
[b]MD/DF calculations, present work.

the higher energy, the (3/1) helix structure leads to a lower energy than the all-*trans* planar zigzag structure, because the intramolecular steric interactions between the methyl side groups are minimized.

To the best of our knowledge, a calculation performing a global optimization of *all* structural parameters of a single *it*-PP chain has not yet been performed. The parameters commonly adopted are $d_{CC}=1.54$ Å, $d_{CH}=1.09$ Å, and bond angles derived from tetrahedral values. An example is the recent exploratory study of single chains of isotactic and two syndiotactic forms of polypropylene, using Hartree-Fock methods[25] to determine the total energies and the energy eigenvalue spectra. Immirzi and Iannelli[26] have used a fiber whole-pattern refinement to analyze x-ray diffraction data. Assuming a chain conformation with fixed bond lengths and three-fold helical symmetry, they obtained C–C–C chain angles of 116.9° and 112.4°, chain dihedral angles of 178° and 59°, and methyl-to-chain bond angles of 108.2°. The refined values are close to those obtained from partial structural optimization using total energy calculations.[27–29]

The present calculations also lead to a (3/1) helix, and the optimized structure has repeat distances along the chain of 6.36 Å and 6.49 Å using LSD and GC approximations, respectively, for the exchange-correlation energy. The LSD structure is then slightly ($\sim$2%) more compressed than the GC structure along the chain, and the repeat distance in the latter is in excellent agreement with the measured value.[13] The other structural parameters, which are reported in Table IV for the case where the repeat distance is constrained to have the experimental value, agree well with the ''standard'' distances and with the optimized angles reported above.[26] The small differences between the optimized LSD structure (repeat distance 6.36 Å) and the constrained values are most evident in the bond angles. If the bond angles in the optimized structures are replaced by the values in Table IV, for example, the repeat period of the chain increases by 0.07 Å. The corresponding changes to the bond lengths and the dihedral angles extend the repeat distance by 0.03 Å and 0.04 Å, respectively.

C. Structural relationships

The qualitative relationship between the different structures is quite evident in Fig. 1. The aim of the present study, however, is to examine the structures in detail and to determine the extent to which the structural parameters—such as

TABLE III. Vibrational frequencies (in cm^{-1}) of conformer (3) of C_5H_{12}.

Experiment[a]	Experiment[b]	SPASIBA[c]	Valence FF[a]	All-electron calculation[d]
		94	84	102
		215	193	210
		227	198	229
		259	204	244
		285	260	263
368		368	365	359
		408	412	411
459		445	461	452
764	764	756	768	754
796		795	793	785
910	911	898	901	889
917	920	928	921	906
952	927	955	958	934
969	977	993	974	944
1011		1019	1008	1001
1037		1037	1039	1050
1149	1150	1150	1146	1139
1176	1158	1175	1168	1157
	1173	1200	1185	1168
1268	1276	1292	1260	1238
1298	1301	1297	1295	1257
1337		1345	1347	1307
1351		1373	1357	1313
1366	1366	1382	1371	1322
1377		1386	1372	1330
1384	1382	1393	1377	1342
	1454	1428	1452	1398
		1447	1458	1402
		1451	1460	1414
		1456	1460	1416
		1459	1462	1423
		1463	1464	1426
	1471	1473	1468	1432
	2883	2859	2855	2948
		2890	2882	2955
		2904	2882	2958
	2891	2908	2883	2964
	2905	2910	2904	2973
		2931	2928	2998
	2958	2967	2960	3033
		2968	2961	3037
		2969	2962	3048
		2969	2962	3049
		2971	2962	3052
	2969	2972	2963	3058

[a]Referemce 20.
[b]Referemce 22.
[c]Reference 21.
[d]Present work.

the bond lengths, and the bond and dihedral angles—are transferable. If the local bonding properties of the polymer chain can be determined reliably by (much more economical) DF calculations on small segments, there is a justifiable hope that the latter can be used to parameterize the forces and energies in the former.

In Table IV we compare the structural features (bond lengths, and bond and dihedral angles) of comparable sections of isotactic polypropylene, $C_{10}H_{22}$, C_5H_{12} (all-electron and MD/DF calculations), and C_3H_8 (ground state with staggered-staggered configuration). Figure 4 shows the labeling of the atoms in a representative section in C_5H_{12}. The bond lengths in the sections of different molecules generally agree well, with substitution of H by CH_3 leading to very small increases in the lengths of C–C bonds at the substituted atoms. The bond angles agree well unless H atoms or C groups are close to other groups containing carbon. This effect can be seen when comparing the C(4)C(3)H(15) bond angle in the molecules, where the open environment of H(15) in C_3H_8 leads to a larger C(4)C(3)H(15) bond angle than in the remaining molecules.

Propane is the smallest and only unbranched molecule amongst those considered, and it is evidently too small to provide accurate estimates of the structural parameters of

TABLE IV. Comparison of structures of sections of isotactic polypropylene (*it*-PP), $C_{10}H_{22}$, C_5H_{12}, and C_3H_8 (bond lengths d in Å, bond angles α and dihedral angles γ in degrees). See Fig. 4 for labeling of atoms.

Parameter	*it*-PP[a]	$C_{10}H_{22}$[b]	C_5H_{12}[b]	C_5H_{12}[a]	C_3H_8[a]
$d_{C_2C_3}$	1.517,1.530	1.529	1.522	1.516,1.524	
$d_{C_2H_{14}}$	1.112,1.098	1.105	1.101	1.109,1.098	
$d_{C_3C_4}$	1.523,1.534	1.531	1.527	1.526,1.531	1.518,1.530
$d_{C_3H_{15}}$	1.113,1.102	1.108	1.104	1.112,1.102	1.106,1.098
$d_{C_3H_{16}}$	1.112,1.099	1.108	1.107	1.114,1.104	1.106,1.098
$d_{C_4C_5}$	1.517,1.529	1.528	1.524	1.518,1.525	
$d_{C_4C_9}$	1.509,1.522	1.524	1.524	1.518,1.525	1.518,1.530
$d_{C_4H_{17}}$	1.112,1.098	1.106	1.106	1.117,1.106	1.107,1.099
$d_{C_5H_{18}}$	1.112,1.099	1.108	1.102	1.109,1.098	
$d_{C_5H_{19}}$	1.112,1.102	1.109	1.105	1.109,1.100	
$d_{C_9H_{27}}$	1.105,1.094	1.101	1.102	1.109,1.099	1.103,1.097
$d_{C_9H_{28}}$	1.105,1.096	1.105	1.102	1.108,1.100	1.106,1.098
$d_{C_9H_{29}}$	1.107,1.094	1.102	1.105	1.109,1.099	1.106,1.098
$\alpha_{C_3C_2H_{14}}$	108.5,108.3	108.5	111.8	111.9,111.9	
$\alpha_{C_2C_3C_4}$	117.5,117.9	116.6	114.0	115.3,114.7	
$\alpha_{C_2C_3H_{15}}$	107.6,107.7	109.1	109.7	109.3,109.2	
$\alpha_{C_2C_3H_{16}}$	109.5,109.3	108.0	110.3	109.9,109.8	
$\alpha_{C_4C_3H_{15}}$	108.2,108.1	108.4	108.5	108.2,108.3	110.7,111.0
$\alpha_{C_4C_3H_{16}}$	107.8,107.8	108.3	108.2	108.1,108.5	110.7,111.0
$\alpha_{H_{15}C_3H_{16}}$	105.5,105.4	105.8	105.9	105.5,106.1	107.0,107.4
$\alpha_{C_3C_4C_5}$	111.5,111.8	111.6	111.7	112.3,112.2	
$\alpha_{C_3C_4C_9}$	109.7,109.8	109.0	110.0	110.8,110.4	110.9,112.6
$\alpha_{C_3C_4H_{17}}$	107.9,107.5	108.2	107.6	107.1,107.6	110.0,109.5
$\alpha_{C_5C_4C_9}$	111.3,111.7	111.3	110.1	110.4,110.2	
$\alpha_{C_5C_4H_{17}}$	108.5,108.3	108.3	108.6	108.0,108.2	
$\alpha_{C_9C_4H_{17}}$	108.0,107.5	108.3	108.7	108.1,108.2	110.0,109.5
$\alpha_{C_4C_5H_{18}}$	109.6,109.2	109.6	112.6	112.3,112.1	
$\alpha_{C_4C_5H_{19}}$	107.7,107.7	107.9	110.0	110.3,110.4	
$\alpha_{H_{18}C_5H_{19}}$	105.5,105.4	106.2	107.8	107.6,107.9	
$\alpha_{C_4C_9H_{27}}$	112.4,112.1	112.3	111.8	111.6,111.3	112.6,111.8
$\alpha_{C_4C_9H_{28}}$	111.4,111.1	110.2	111.6	111.8,110.5	110.7,111.0
$\alpha_{C_4C_9H_{29}}$	110.5,111.4	111.0	110.0	110.4,111.5	110.7,111.0
$\alpha_{H_{27}C_9H_{28}}$	107.6,107.3	107.9	108.1	107.9,107.6	107.8,107.7
$\alpha_{H_{27}C_9H_{29}}$	107.4,107.3	107.8	107.6	107.3,108.1	107.8,107.7
$\alpha_{H_{28}C_9H_{29}}$	107.4,107.4	107.5	107.6	107.5,107.7	107.0,107.4
$\gamma_{C_2C_3C_4C_5}$	−61.6,−59.8	−60.0	−63.2, 0	−62.6,−63.1	
$\gamma_{C_2C_3C_4C_9}$	174.8,175.6	176.6	174.2	173.4,173.7	
$\gamma_{C_3C_4C_9H_{27}}$	−175.8,−173.5	−176.1	−178.7	−178.0,−178.1	−180.0,−180.0
$\gamma_{H_{14}C_2C_3C_4}$	63.8,59.9	63.9	63.6	63.4,63.8	
$\gamma_{H_{17}C_4C_5H_{19}}$	−173.4,−177.4	−175.5	−177.6	−177.7,−177.9	

[a]Present work, pseudopotential calculations (LD and GC results, respectively).
[b]Present work, all-electron calculations (Ref. 17), LD approximation. In $C_{10}H_{22}$ the C(1)-C(7) distance was constrained to be the measured period of the *it*-PP chain (6.5 Å, Ref. 13).

larger hydrocarbons. The additional C atoms in isopentane and the higher steric strain result in a structure that agrees better with those of $C_{10}H_{22}$ and *it*-PP.

We have noted above that conformer (3) of isopentane is more stable than conformer (3, rotated methyl) by 3.07 kcal mol^{-1}. Figure 2 shows that these molecules are propane-like sections in staggered-staggered [IP(3)] and staggered-eclipsed [IP(3, rotated methyl)] configurations. We might then expect that the energy difference between these two conformers should be similar to the energy difference between staggered-staggered and staggered-eclipsed forms in propane, for which the experimental value is 3.17 kcal mol^{-1} (Ref. 30) and LSD calculations give 3.1 kcal mol^{-1} (Ref. 8). The excellent agreement between isopentane and propane results shows the transferability of energy differences in this case as well. We have also performed all-electron calculations on $C_{10}H_{22}$ with a comparable methyl group rotated by 60°. The energy difference between this structure and the structure without methyl rotation (3.03 kcal mol^{-1}) also agrees well with the results for methyl group rotation in isopentane and propane.

IV. DISCUSSION AND CONCLUDING REMARKS

We have extended our earlier density functional (DF) calculations on small hydrocarbon molecules to larger systems, including isomers of isopentane and a single chain of isotactic polypropylene (*it*-PP). The calculations have been of two types: (a) DF calculations with simulated annealing, using a pseudopotential description of the electron-ion and a plane-wave basis set, and (b) DF calculations with a localized, Gaussian basis set, which consider all electrons. The

agreement between the two sets of calculations is very good. Calculations have been performed with both LSD and gradient-corrected approximations to the exchange-correlation energy. A particular focus has been the relationship between the structures and energy differences in larger systems, such as isotactic polypropylene or $C_{10}H_{22}$, and smaller molecules with closely related structures.

We have optimized the structures of five conformers of isopentane. The overall picture is consistent with the results of an earlier Hartree-Fock study, and the most stable form [IP(3)] is that which arises in the chain structure of *it*-PP. The latter is helical (3/1), with 27 atoms in the unit cell, and the structure optimized using the LSD approximation has a repeat distance along the chain that is $\sim 2\%$ shorter than that found in x-ray diffraction studies.[13] The GC energy functional leads to excellent agreement with the experimental repeat distance (6.50 Å). The GC functional leads to C–C bonds that are slightly longer than in the LSD calculations and in good agreement with the ''standard'' value assumed for C–C single bonds.

With the exception of propane, there is a remarkable transferability of the structural parameters between molecules with the same local environment. This is very encouraging, as it indicates that the results of DF calculations for small structural units should be useful for predicting the energy surfaces of larger organic molecules. It is not surprising that the structural parameters for propane differ from those of the other molecules, all of which are branched. On the other hand, the differences are not large even in this case, and are most apparent in the bond angles.

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