Ab-Initio and PCILO Calculations of Diamond Clusters and the Corresponding Saturated Hydrocarbons

H. P. Waschi, H. Stoll and H. Preuß
Institut für Theoretische Chemie der Universität Stuttgart

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Closed-shell diamond clusters and saturated hydrocarbons are investigated with PCILO and ab-initio Hartree-Fock using very small basis sets. The ab-initio distances for the C–C bonds differ by 5% or less, the PCILO distances by 2 to 2.5% from experimental data. The dependence of bond lengths and force constants on the cluster construction is studied. For selected molecules the effect of intermolecular rotations on the total energy is considered.

1. Introduction

Simple molecules with one first-row atom can be calculated almost exactly by the methods of quantum chemistry. For molecules with several first-row atoms or with a second-row atom the computational effort rises steeply. However, by attaching importance to a qualitative comparison of the properties of different compounds similar to each other, the computing effort can be restricted, using a relatively small set of basis functions. Thus estimations of, — for example, effects of substituents or conformation probabilities can be obtained with comparatively small expenditure.

This paper concerns research done on the development of bond lengths and force constants of diamond clusters and the corresponding saturated hydrocarbons with increasing size and perfection of the crystal structure, assuming a closed-shell wavefunction.

The smallest of the computed fragments of the diamond lattice correspond with the carbon skeletons of simple organic molecules as cyclohexane or neopentane. The largest fragment consists of 22 carbon atoms.

To retain the surroundings existing in the diamond lattice as invariant as possible for the cluster atoms, it is necessary to construct the clusters by keeping the bond lengths and angles identical everywhere, and by surrounding the carbon atoms tetrahedrally by neighbour-atoms to a very high extent. That is, six atoms are best grouped together not in a linear manner but as a six-membered ring, additional atoms or rings are added in the third dimension with regard to the ring plane. Also, the hydrogen bonds of the saturated hydrocarbons were arranged tetrahedrally and not varied individually. The conformational behavior was analysed in a separate investigation if degrees of freedom — concerning rotation around a bond — occured after the adjustment of the molecular structure.

All the molecules out of the multitude of carbon compounds with at most 20 carbon atoms which fitted the given criteria are shown in Fig. 1 as saturated hydrocarbons with staggered bonds, and are

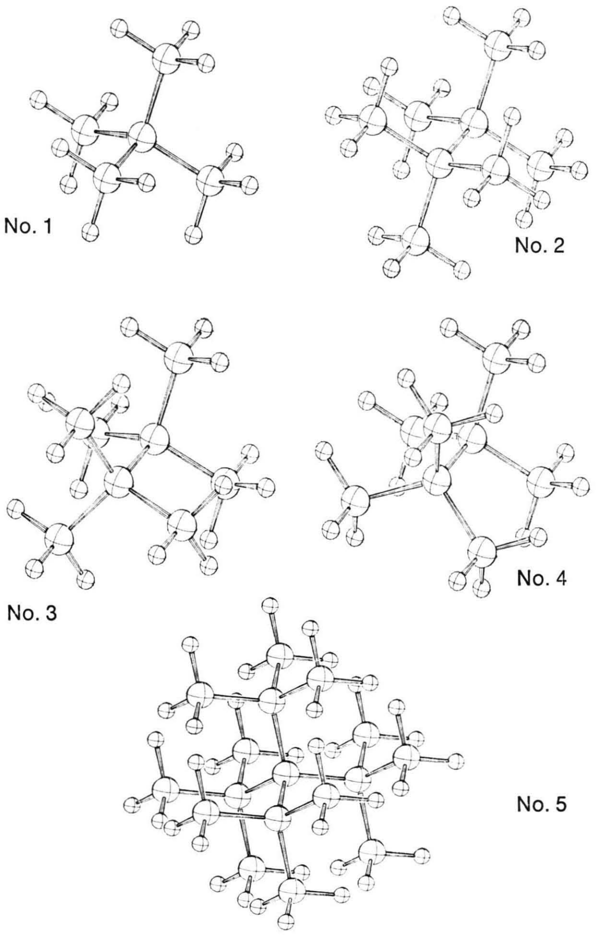

Fig. 1. Computed saturated hydrocarbons.

Reprint requests to H. P Waschi, Institut für Physikalische Chemie der Universität, Pfaffenwaldring 55, D-7000 Stuttgart 80

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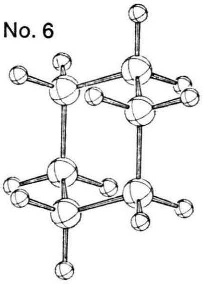

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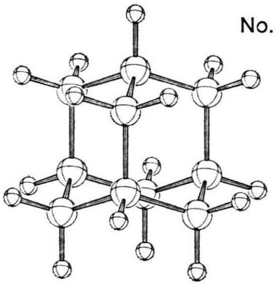

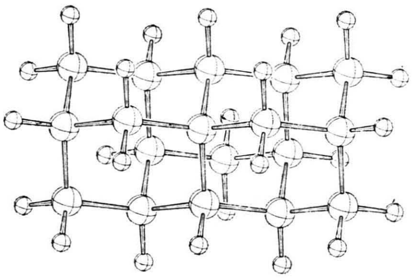

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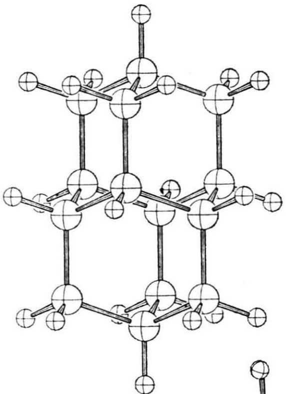

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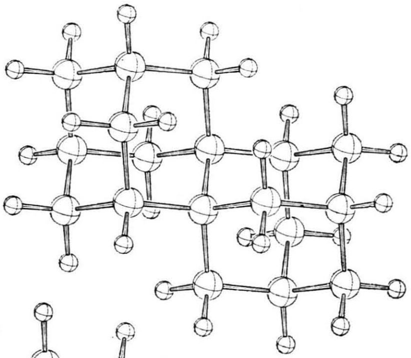

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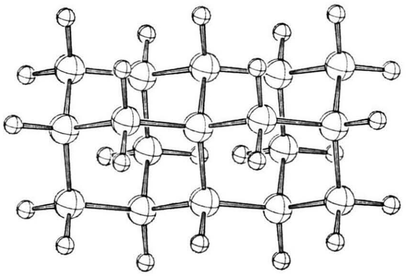

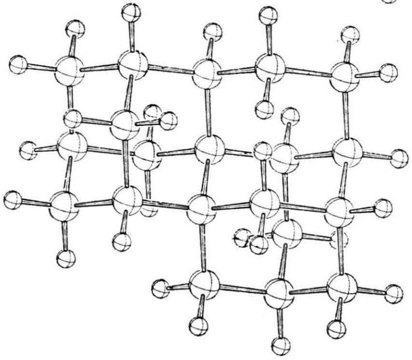

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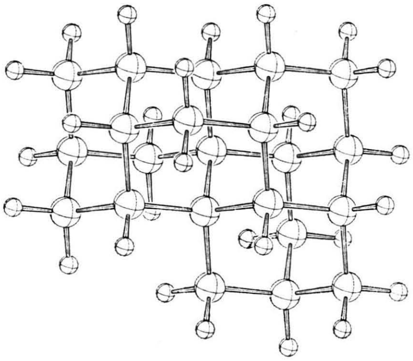

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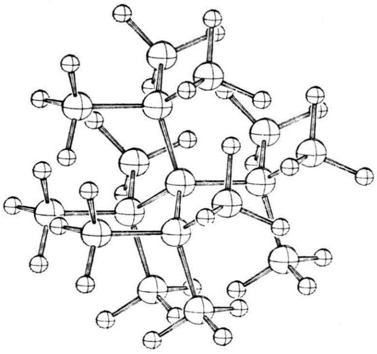

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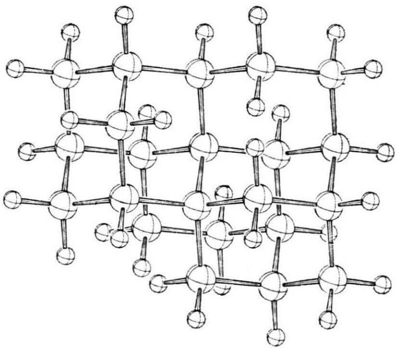

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designated with Arabic numerals. The non-saturated diamond clusters have the same numbering as the hydrocarbons that correspond to them but are designated in the text with Roman numerals.

By arranging a spherical shell of four neighbouring carbon atoms around a central carbon atom, neopentane (No. 1, C_5H_{12}) as the simplest investigated compound is obtained. An additional shell of the twelve next neighbouring atoms produces molecule No. 5 ($C_{17}H_{36}$). Molecules No. 2 to 4 (C_8H_{18}), which counter-rotate around the central C—C bonding by 30° relative to each other hold an intermediate position and can be regarded as neopentane with a t-butyl substituent, thus constituting the first step from No. 1 to No. 5. They serve the study of the most favourable arrangement sterically of atomic groups which are not fixed by a six-membered ring.

The disadvantage of spherical fragments of diamond crystals is a low quota of quarternary carbon atoms (i.e. 30% for molecule No. 5). The quota could be raised to 77% by adding a third shell. In that way the first molecule of that kind with six-membered rings would be produced. This molecule however, could not be computed.

To produce further molecules it is therefore advisable to build them out of six-membered rings in chair configuration (molecule No. 6, C_6H_{12}), connected to each other with as many bonds as possible. By that method, diamond-like structures are achieved much faster, as adamantane (No. 7, $C_{10}H_{16}$), the next molecule in order, has shown.

The construction of even larger systems can be achieved in two ways, both producing a group of molecules. The molecules of these two groups are in a clearly significant hierarchic order. In the first variant, adamantane cells are connected by a common face which leads to molecules No. 8 (diamantane, $C_{14}H_{20}$), No. 10 (triamantane, $C_{18}H_{24}$) and No. 13 ($C_{22}H_{28}$). If the other variant of construction is used, two adamantane units are connected by a common edge (No. 11, $C_{18}H_{26}$) and the following connections are achieved by adding two carbon atoms with each step. This addition produces a new six-membered ring: No. 12 ($C_{20}H_{28}$) and No. 14 ($C_{22}H_{30}$).

Two adamantane units with two common edges are shown by the molecule No. 9 ($C_{17}H_{24}$) which does not belong to either group.

Even with limitation to the smallest basis sets these very large molecules could not be managed with ab-initio methods, therefore the ab-initio treatment had to be restricted to the smaller molecules. For that purpose the programs MOLPRO by Meyer and Pulay [1] and ELEMOT by Janoschek [2] were used. The Gaussian basis sets chosen are given in Table 1. These basis sets were used as well in another ab-initio programm (LOSD1) written by us [5]. It shortens the computation time by splitting the total system into subsystems with comparatively few orbitals and a corresponding partitioning of the basis set *.

Table 1. Basis sets for the ab-initio calculations.

Carbon functions					
(2s1p)[a]			9.407	0.3038 /	0.3545
(3s1p)		46.68	6.781	0.335 /	0.3552
(4s2p)[a]	156.7	23.54	5.039	0.2998 / 1.556	0.2795
Hydrogen functions					
(2s)[b]			1.33248	0.201527	

[a] Ref. [3]; [b] Ref. [4].

To cover a satisfactory number of great molecules calculations with the semi-empirical PCILO method [6] were performed also. In our version, we could deal with closed-shell problems only. As it is known, the Slater determinant in this method is constructed from bond orbitals. Therefore, non-saturated diamond clusters could not be investigated.

The bond lengths and force constants of the examined molecules were taken from the energy hypersurface constructed from LOSD1 and PCILO calculations respectively. These values moreover, were claculated with MOLPRO by means of the "force method" [7].

2. Calculations of Diamond Clusters

For the reasons given above these molecules were calculated only ab-initio by way of the Hartree-Fock procedure. For the smallest cluster (No. I) all uncontracted basis sets of Table 1 could be used. Proceeding from a (3s1p) basis of Whitman and Hornback, optimized for atoms, the optimization

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* This program however was used for the calculation of neopentane only, for the purpose of testing the effects of various approximations with a large molecule.

of this basis set for molecules showed that the s-function with the smallest η-value has the strongest influence upon the total energy. Thus, in the lattice, the diffuse functions of the neighbouring atoms serve for the description of the dominant cores, that is, the effect of basis superposition plays a considerable part. With this (3s1p) basis the molecules II to IV were calculated. With molecule No. VII only the (2s1p) basis was left for consideration.

Table 2 shows the energy of a single carbon atom for the applied basis sets. The binding energies in Table 3 represent the difference between the energy of the isolated atom and the total energy of the molecular system in respect to one atom.

Basis set	Energy
(2s1p)[a]	− 32.01619
(3s1p)[a]	− 36.28441
(3s1p)[b]	− 36.28009
(4s2p)[a]	− 37.35565
(5s2p)[a]	− 37.51312
Hartree-Fock[a]	− 37.68861

Table 2. Carbon total energies in atomic units for Gaussian-type basis sets.

[a] taken from Ref. [3], optimized for atoms;
[b] optimized for cluster No. I.

Using the forces method, the force constant matrix must be known for the calculation of the bond distances. An improved force constant matrix obtained from the original starting matrix needs two iteration steps. Thus the bond lengths and force constants calculated by this method converge after several iterations only. As the bond distances — with exception of the smaller basis sets for the molecule No. I — were computed with one forces calculation only, force constants for the C—C bonds cannot be given in Table 3 in general. The distances computed in this manner are shorter than those computed for a complete convergence. $r = 1.543$ [Å] and $\varkappa = 5.0$ [mdyn/Å] were chosen as starting parameters.

For reasons of comparison the properties of molecule I as calculated from the hypersurface are given in Table 3 also.

For molecule I a decreasing binding energy with increasing quality of the basis set can be observed. A (11s5p) basis contracted to (4s3p) leads to a positive value for the binding energy [10]*.

Table 3 also shows an energetic preference of a sic-membered ring arrangement in comparison to arrangements which contain many atoms with only one nearest neighbour.

With all conformations of the C_8-cluster the length of its central bond is in good agreement with experiment, being in a surrounding very similar to that of diamond because of the spatial enveloping by neighbour atoms. The reduction of the bond

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* This applies for the closed-shell wavefunction. UHF calculations show a distinct dependence of the cluster properties on the total spin of the system. A far-reaching correspondence of the computed properties of the central atom with those of the infinite crystal exists for the total spin S = 6. Here the total energy becomes negative again [10].

Table 3. Ab-initio results for diamond clusters. Units in Å, mdyn/Å and atomic units, respectively.

Cluster	(2s1p)			(3s1p)			(4s2p)		exp.	
	r_{C-C}	$\varkappa_{C-C}$	E_{bind}/atom	r_{C-C}	$\varkappa_{C-C}$	E_{bind}/atom	r_{C-C}	E_{bind}/atom	r_{C-C}	$\varkappa_{C-C}$
I	1.491[a]	12.19[a]	− 0.128	1.533[a]	8.67[a]	− 0.056[b]	1.516	− 0.021		
	1.482[c]	13.71[c]		1.533[c]	8.89[c]					
	1.481[d]	9.98[d]		1.532[d]	7.93[d]					
II[e]				1.543		− 0.050				
				1.597						
III[e]				1.543		− 0.056				
				1.597						
IV[e]				1.543		− 0.060				
				1.549						
VI	1.493		− 0.202							
VII	1.586		− 0.199							
C									1.5445[f]	4.5[g]

[a] Obtained by two iterations of the forces calculation;
[b] for this value, the cluster-optimized basis was used;
[c] obtained by three iterations of the forces calculation;
[d] obtained from energy hypersurface;
[e] the first bond distance refers to the rotation axis between the two halves of the molecule, the second one refers to the other C—C bonds;
[f] measured for diamond, Ref. [8];
[g] mean value for alkanes, Ref. [9].

length of the outer atoms with progressive rotation can be explained from an increasing overlap between the two halves of the molecule. For the forces calculations leading to these results a common potential minimum was assumed.

3. Saturated Hydrocarbons

The dihedral angles of the C—H bonds are fixed for the cyclic hydrocarbons by the assumption of sp^3-hybrid orbitals for the carbon atoms. PCILO calculations of compounds with methyl groups show the staggered arrangement of all C—H bonds as the most favourable for molecule No. 1. Molecules No. 2 to 4 were arranged accordingly. The most probable conformation for molecule No. 5 appears with the dihedral angle of 29.5° * (cf, No. 15, Fig. 1).

All compounds given in Fig. 1 were calculated with PCILO. Their computed properties (Table 4) reproduce exactly the classification into different groups resulting from the construction of the molecules as shown in sec. 1. In the calculation of the bond distance all C—C or C—H bonds were treated as linear combinations. So the bond lengths of the molecules 2 to 5 have to be different from those of neopentane because not all of the bonds are in the identical surrounding in these molecules. All C—H bonds of this group are in a similar surrounding with the exception of molecule No. 5 where the hydrogen atoms of different t-butyl groups are closer to each other than those of the same methyl group. Therefore these bonds are shortened and the C—C bonds of this compound are extended.

All C—H bonds of the group represented by the molecules No. 7, 8, 10, 13 are of the same size. The carbon skeletons of these molecules are suitable

Table 4a. Results of PCILO calculations. Units in Å, mdyn/Å and debye respectively.

Molecule	Formula	r_{C-C}	$\varkappa_{C-C}$	r_{C-H}	$\varkappa_{C-H}$	$\mu \cdot 10^2$
1	C_5H_{12}	1.502	16.97	1.131	11.26	—
2	C_8H_{18}	1.515	17.81	1.131	11.25	—
3	C_8H_{18}	1.514	17.57	1.132	11.18	—
4	C_8H_{18}	1.517	17.74	1.131	11.25	—
5	$C_{17}H_{36}$	1.598	19.18	1.123	11.53	—
6	C_6H_{12}	1.496	16.77	1.137	10.83	—
7	$C_{10}H_{16}$	1.511	17.43	1.138	10.79	—
8	$C_{14}H_{20}$	1.517	17.73	1.138	10.76	—
10	$C_{18}H_{24}$	1.520	17.78	1.138	10.71	3.4
13	$C_{22}H_{28}$	1.523	17.77	1.138	10.67	8.9
7	$C_{10}H_{16}$	1.511	17.43	1.138	10.79	—
11	$C_{18}H_{26}$	1.520	17.84	1.137	10.85	—
12	$C_{20}H_{28}$	1.537	18.53	1.120	12.97	18.2
14	$C_{22}H_{30}$	1.547	18.82	1.109	14.33	24.3
9	$C_{17}H_{24}$	1.537	17.88	1.118	13.09	16.6

Table 4b. PCILO energies and energy corrections in kcal.

No.	$E_0 \cdot 10^{-}$	$E_D \cdot 10^{-2}$	$E_{intra} \cdot 10^{-2}$	$E_{inter} \cdot 10^{-2}$	$\sum E^{(2)} \cdot 10^{-2}$	$E^{(2)}_{total} \cdot 10^{-4}$	$\sum E^{(3)} \cdot 10^{-2}$	$E^{(3)}_{total} \cdot 10^{-4}$
1	– 2.80345	– 1.362	– 0.978	– 0.299	– 2.639	– 2.82984	0.253	– 2.82731
2	– 4.42911	– 2.343	– 1.525	– 0.585	– 4.453	– 4.47364	0.603	– 4.46761
3	– 4.42885	– 2.392	– 1.528	– 0.579	– 4.499	– 4.47384	0.621	– 4.46763
4	– 4.42832	– 2.384	– 1.527	– 0.595	– 4.506	– 4.47338	0.631	– 4.46707
5	– 9.25705	– 5.813	– 3.230	– 1.691	–10.734	– 9.36439	1.673	– 9.34766
6	– 3.25343	– 2.063	– 1.086	– 0.414	– 3.563	– 3.28906	0.301	– 3.28605
7	– 5.23865	– 3.097	– 1.661	– 0.925	– 6.493	– 5.30358	1.014	– 5.29344
8	– 7.22389	– 5.698	– 2.236	– 1.448	– 9.382	– 7.31771	1.732	– 7.30039
10	– 9.20896	– 7.483	– 2.811	– 1.990	–12.284	– 9.33180	2.501	– 9.30679
13	–11.19345	– 9.268	– 3.390	– 2.558	–15.216	–11.34561	3.297	–11.31264
7	– 5.23865	– 3.907	– 1.661	– 0.925	– 6.493	– 5.30358	1.014	– 5.29344
11	– 9.29965	– 7.267	– 2.889	– 1.916	–12.072	– 9.42037	2.325	– 9.39712
12	–10.27929	– 7.764	– 3.131	– 2.226	–13.121	–10.41050	2.505	–10.38545
14	–11.26062	– 9.406	– 3.387	– 2.536	–14.329	–11.40351	2.751	–11.37600
9	– 8.74551	– 6.550	– 2.660	– 1.845	–11.055	– 8.85606	2.004	– 8.83602

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* This angle was determined before the optimization of the bond distances.

fragments of the diamond lattice, as there are no carbon bridges projecting from the cluster. The surroundings of the hydrogen atoms which envelope these clusters like a membrane are practically not dependent any more on the size of the clusters fitting to the construction criteria of this group. Therefore it can be assumed that the C—H distance of 1.138 [Å] is in accordance with the bond distance of hydrogen atoms on the surface of a diamond crystal. This far-reaching identity of the carbon clusters is confirmed by the C—C distance which rises only slowly.

With increasing size the molecules of the next series (No. 7, 11, 12, 14) lose their compactness, containing more and more atoms in different surroundings. Therefore these bond lengths deviate progressively from those of the group described above.

According to their calculation from the breathing vibration of the molecules the force constants are again reproducing the distinction into various groups.

In Table 4b the denotation of the important components of the second order energy correction $\sum E^{(2)}$ is as follows: monoexcitation between two bonds (delocalization energy): E_{D}, diexcitation in one bond (intra bond correlation energy): E_{intra}, monoexcitation in one bond (interbond correlation energy): E_{inter}. Being smaller than the total energy by 10 orders of magnitude, the polarisation energy is not listed in Table 4b. The third order energy correction $\sum E^{(3)}$ is not subdivided into components because all terms containing polarisation are practically of no importance.

By way of example for molecules No. 2 to 4 Fig. 2 shows the energy behaviour of No. 2 as a function of the rotation angle α around the central C—C bond. The energy minimum is given at an angle of $\alpha = 25°$ out of the staggered conformation. The maximum energy is 5.7 [kcal] higher at $\alpha = 60°$ (eclipsed conformation). Between the staggered conformation and $\alpha = 25°$ an energy plateau lies at about 0.28 [kcal] above the minimum.

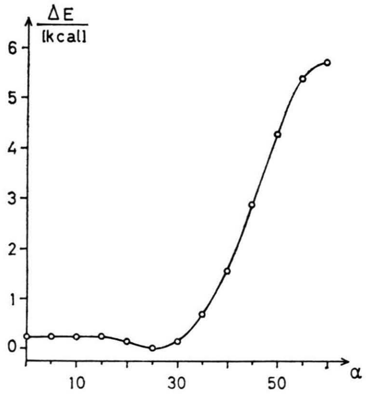

Fig. 2. Rotation of molecule No. 2 around the central bond.

For the interpretation of this curve the consideration of two relative motions is sufficient: the carbon atoms of different halves of the molecule approach with progressing α with the strongest repulsion at $\alpha = 60°$. The next-neighboured hydrogen atoms of two different halves withdraw from each other until they have reached their greatest distance at about $\alpha = 30°$. With still increasing α their distance becomes even shorter than at the starting point. During the first part of the rotation the energy increases for the first motion, and decreases for the second. The resultant total energy is almost constant. During the second part, the energy increases for each motion, resulting in an increased total energy. Therefore the location of the energy minimum at $\alpha = 25°$ can be explained qualitatively for all three molecules, even though their bond lengths differ slightly. The explanation is that an alteration of the total energy caused by a deflection out of the potential minimum of 10^{-3} [Å] is smaller than the difference between the energy plateau and the minimum of the curve by more than one order of magnitude.

Only molecules No. 1 and 6 in connection with the (2s1p/2s) basis set were suitable for the ab-initio calculation of the saturated hydrocarbons*. The optimization of the geometry was done via the energy hypersurface with LOSD1 and via the forces method with the HF program. In the latter case the calculations included only one iteration respectively, according to the calculations on diamond clusters (sec. 2) and with the consequences on the results as described there. The starting parameters were taken unchanged from the diamond clusters for the C—C bonds, for the C—H bonds they ran as $r_{\mathrm{C-H}} = 1.070$ [Å] and $\varkappa_{\mathrm{C-H}} = 5.0$ [mdyn/Å].

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* In the LOSD1 program the functions were distributed as lobes over the following subsystems:

- the carbon atoms with the contracted functions $\eta_1 = 9.407$ and $\eta_2 = 0.3038$,
- the centers of the C—C bonds with $\eta = 0.3545$,
- the hydrogen atoms and the centers of the respective C—H bonds with the two hydrogen functions of Table 1 and with the function $\eta = 0.3545$ situated on the bond-midpoint.

Table 5. Calculated and measured values (by electron diffraction) of some hydrocarbons. Units in Å and mdyn/Å, respectively.

		PCILO	HF	LOSD1	exp.
No. 1 C_5H_{12}	r_{C-C}	1.502	1.603	1.651	1.533[a], 1.539[b]
	$\varkappa_{C-C}$	16.97		15.49	4.3[c]
	r_{C-H}	1.131	1.213	1.172	—
	$\varkappa_{C-H}$	11.26		8.06	4.7[c]
No. 2 C_8H_{18}	r_{C-C}	1.515			1.580[a,d]
	$\varkappa_{C-C}$	17.81			4.3[c, d]
	r_{C-H}	1.131			—
	$\varkappa_{C-H}$	11.25			4.7[c]
No. 6 C_6H_{12}	r_{C-C}	1.496	1.595		1.534[f]
	$\varkappa_{C-C}$	16.77			4.5[c]
	r_{C-H}	1.137	1.210		1.103–5[f]
	$\varkappa_{C-H}$	10.83			4.7[c]
No. 7 $C_{10}H_{16}$	r_{C-C}	1.511			1.540[g]
	$\varkappa_{C-C}$	17.43			—
	r_{C-H}	1.138			1.112[g]
	$\varkappa_{C-H}$	10.79			4.7[c]

[a] Ref. [11]; [b] Ref. [12];

[c] Ref. [13]. The given values are mean values for the type of bonding;

[d] This value holds for the central C—C bond;

[e] Ref. [14]; [f] Ref. [15].

The results of these calculations are shown in Table 5 where they are compared with the existing experimental data.

4. Conclusion

The ab-initio calculation of small closed-shell diamond clusters with very small basis sets yields bond lengths which differ from the diamond value by 5% or less. Poor results, on the other hand, were obtained for the force constants of the C—C bonds which were too great. The force constants computed from the energy hypersurface turned out to be more exact than those from forces calculations. The binding energies showed a preference of ring structures in comparison to clusters where some atoms are without two binding partners within the same distance. These clusters strive for a geometry which does not correspond to that of the diamond lattice. Apart from geometry alterations by rotation which cancel out the fully staggered arrangement of all bonds, this holds for the tetrahedral angle too. This can be concluded from the two different bond lengths of the clusters No. 2 to 4 which resulted from the calculations, though all bonds were expanded in a coupled manner.

The binding energy of the C_5 closed-shell cluster decreases with enlarging basis set and finally vanishes. A comparative computation with the energetically more favoured C_6 cluster could not be performed.

The properties and energy corrections of the hydrogen saturated clusters calculated with PCILO show a strong geometry dependence. The most effective structure is the one resulting from a compact fragment of the diamond lattice, constructed from six-ring units. For such a structure, the results converge with increasing size. So they suggest an extrapolation to the properties of the infinite crystal — with the restriction that with this program the bond distances show a systematic error. Also the force constants are too large throughout.

A divergence from the principles of construction of this group is expressed by a change of the bond lengths and accordingly the force constants. This is the case for the molecules No. 9, 12, 14 especially. Also the combination of several steric relative motions was reproduced exactly by the total energy.

In comparison with the results from the experimental data, the C—C distances from the PCILO calculations are too short for 2 to 2.5% (with the molecule No. 2 a comparison is not possible). The C—H distances cannot be compared among each other because there are secondary and tertiary bonds in the molecule No. 7.

On the other hand the ab-initio distances turned out too long. As far as there exist results the factor for the distance of two carbon atoms is 4 to 4.5% with the HF program. With LOSD1 the deviation is even larger. The relatively good description of the C—H bond with this program is caused by the choice of the subsystems.

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