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Letter

The equilibrium structures of linear carbon clusters of type C_{2n+1} (n = 1–4)

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Abstract. On the basis of large-scale coupled-cluster calculations including connected triple substitutions accurate equilibrium structures have been established for the linear carbon chain molecules with an odd number of carbon atoms up to C_9. The individual equilibrium bond lengths are indicative of strong double bonds in all cases.

Key words: Linear carbon clusters – Equilibrium structures

The determination of accurate equilibrium structures solely on the basis of experimental data continues to be a difficult task even for small molecules. The situation is particularly awkward when the molecule of interest has no permanent dipole moment and is thus not accessible to microwave and millimeter-wave spectroscopy. Interesting species of this kind are the linear carbon clusters which have attracted much interest over the past two decades [1, 2]. Even in the case of C_3, the determination of an accurate experimental equilibrium structure causes problems which are connected with the extremely shallow bending potential; therefore, the best CC equilibrium bond length for linear centrosymmetric C_3 available in the literature was obtained by a mixed experimental/theoretical procedure where the ground-state rotational constant, B_o, was taken from experiment and the difference, $B_e - B_o$, was calculated variationally from a high-quality ab initio potential-energy function [3]. Here, B_e stands for the equilibrium rotational constant, whose square root is inversely proportional to the CC equilibrium separation. The resulting R_e value was 1.2936 Å.

In this letter accurate equilibrium geometries are reported for closed-shell linear carbon clusters of type C_{2n+1} up to $n = 4$. These are obtained from coupled-cluster calculations with large basis sets plus corrections for systematic errors. The well-established variant CCSD(T) [4] is mainly employed in the calculations, which were carried out with the MOLPRO98 suite of programs [5–7].

Following our earlier work on linear C_5 [8, 9] within the coupled-electron-pair approximation (CEPA-1) [10] and at the CCSD(T) level with basis sets up to correlation-consistent polarized valence quadruple zeta (cc-pVQZ) [11], the equilibrium structure of this species was calculated by CCSD(T) with the large correlation-consistent polarized core–valence quadruple-zeta (cc-pCVQZ) basis set of Woon and Dunning [12], which comprises 420 contracted Gaussian-type orbitals (cGTOs). All electrons were correlated in these calculations. The results are R_{1e} (outer CC) = 1.2901 Å and R_{2e} (inner CC) = 1.2828 Å. The corresponding equilibrium rotational constant is B_e = 2547.7 MHz and it may be compared with an approximate experimental value of 2548.7 MHz [13]. CCSD(T) calculations with the cc-pCVQZ basis have a tendency to slightly overestimate R_e values for multiple CC or CN bonds, for example, R_e (CN) of HCN is overestimated by 0.0006 Å [14]. Likewise, the CC equilibrium bond length of 1.2037 Å calculated for HCCH is longer than the recommended value of Martin et al. [14] by 0.0009 Å. CCSD(T) calculations with the cc-pCVQZ basis for C_3 yield R_e = 1.2946 Å, 0.0010 Å longer than the above mixed experimental/theoretical value. We therefore employ a mean value of 0.0008 Å to correct the CC equilibrium bond lengths obtained by CCSD(T)/cc-pCVQZ. The recommended equilibrium structure for C_5 is thus R_{1e} = 1.2893(4) and R_{2e} = 1.2820(4) Å, with estimates of the errors in terms of the least significant digit being given in parentheses. The corresponding B_e value is 2550.8 MHz, which is still very close to the approximate experimental value. The author's previous CCSD(T) calculations [9] with the cc-pVQZ basis [11] in which all electrons were correlated yielded R_{1e} = 1.2896 Å, R_{2e} = 1.2819 Å and B_e = 2550.6 MHz.

CCSD(T) calculations with the cc-pCVQZ basis are rather time-consuming for C_{2n+1} species with $n \geq 3$. For C_7 and C_9 we therefore make use of the cc-pVQZ basis and correlate only the valence electrons. For C_5, such calculations yield R_{1e} = 1.2936 Å and R_{2e} = 1.2857 Å. They differ from the recommended values by 0.0043 and 0.0037 Å, respectively, where the major part of the

Table 1. Calculated equilibrium bond lengths, total energies and equilibrium rotational constants for linear C_7. Basis: cc-pVQZ (385 cGTOs). Valence electrons are correlated in the post-Hartree–Fock calculations. In this table and the following ones, the carbon–carbon bonds are numerated from outermost to innermost

Method	R_{1e} (Å)	R_{2e} (Å)	R_{3e} (Å)	V_e (E_h)	B_e (MHz)
SCF	1.2622	1.2744	1.2575	−264.775081	940.6
MP2	1.2938	1.2898	1.2756	−265.850640	911.5
CCSD	1.2809	1.2840	1.2688	−265.815857	923.2
CCSD-T	1.2930	1.2901	1.2758	−265.904786	911.5
CCSD(T)	1.2934	1.2903	1.2760	−265.905998	911.1
Corr.[a]	1.2894	1.2863	1.2720		916.8[b]

[a] Previous recommended equilibrium structure [17]: $R_{1e} = 1.290$ Å, $R_{2e} = 1.286$ Å and $R_{3e} = 1.272$ Å
[b] Experimental ground-state value: $B_o = 917.80$ (44) MHz [18]

Table 2. Calculated equilibrium bond lengths, total energies and equilibrium rotational constants for linear C_9. Basis: cc-pVQZ (495 cGTOs). Valence electrons are correlated in the post-Hartree–Fock calculations

Method	R_{1e} (Å)	R_{2e} (Å)	R_{3e} (Å)	R_{4e} (Å)	V_e (E_h)	B_e (MHz)
SCF	1.2611	1.2779	1.2548	1.2629	−340.464112	349.6
MP2	1.2944	1.2922	1.2748	1.2797	−341.868918	426.3
CCSD	1.2802	1.2860	1.2666	1.2731	−341.811380	431.7
CCSD-T	1.2927	1.2926	1.2743	1.2797	−341.927952	426.5
CCSD(T)	1.2930	1.2927	1.2745	1.2798	−341.929305	426.4
Corr.	1.2890	1.2887	1.2705	1.2758		429.1[a]

[a] Experimental ground-state value: $B_o = 429.34$ (3) MHz [19]

Table 3. Recommended equilibrium structures for linear species of type C_{2n+1}. Estimated uncertainties in terms of the least significant digit are given in parentheses

n	Carbon–carbon equilibrium bond lengths (Å)				B_o (exp.)/B_e^a
1	1.2936 (4)				1.0258
2	1.2893 (4),	1.2820 (4)			1.0027
3	1.2894 (6),	1.2863 (6),	1.2720 (6)		1.0011
4	1.2890 (6),	1.2887 (6),	1.2705 (6),	1.2758 (6)	1.0006

[a] For experimental B_o values see Refs. [18–20]

differences is attributed to the neglect of core–valence correlation effects. We use a mean value of 0.0040 Å as a correction for the larger clusters. Results of geometry optimizations for C_7 and C_9 (under the well-founded assumption of centrosymmetric linear equilibrium structures) are given in Tables 1 and 2 which also include the results obtained by MP2, CCSD [16] and CCSD-T [7] calculations. The present recommended equilibrium structure for C_7 is in excellent agreement with our previous estimate [17], which was based on CCSD(T) calculations with a basis of 238 cGTOs. The equilibrium rotational constant of C_7 is predicted to be 916.8 MHz, with an estimated uncertainty of 0.8 MHz. The experimental ground-state value (Table 1, footnote b) is slightly larger.

The two outermost CC equilibrium bond lengths of C_9 are almost identical and practically coincide with the outermost R_{1e} of C_7. R_{3e} (C_9) is the shortest. The inclusion of connected triple substitutions in the coupled-cluster calculations is mandatory in order to obtain the correct order of the equilibrium bond lengths. Connected triple substitutions increase R_{1e} by as much as 0.013 Å, while $R_{2e} - R_{4e}$ experience elongations by only about half this value. As for C_7, the MP2 results are surprisingly close to those obtained by CCSD(T) or CCSD-T. The later two methods produce very similar results for all the carbon clusters which have been studied in this work. The recommended B_e value for C_9 is 429.1 MHz, again slightly below the experimental B_o value (Table 2, footnote a).

The recommended equilibrium structures for linear carbon clusters of type C_{2n+1} up to C_9 are summarized in Table 3 together with estimates of the uncertainties in the equilibrium bond lengths. This table also contains the ratios B_o (experimental)/B_e. There is a significant deviation from unity for floppy C_3, while B_o and B_e become increasingly similar with increasing chain length.

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