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Molecular Structure of the Octatetranyl Anion, C_8H^-: A Computational Study

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The equilibrium molecular structure of the octatetranyl anion, C_8H^-, which has been recently detected in two astronomical environments, is investigated with the aid of both ab initio post-Hartree−Fock and density functional theory (DFT) calculations. The model chemistry adopted in this study was selected after a series of benchmark calculations performed on molecular acetylene for which accurate gas-phase structural data are available. Geometry optimizations performed at the CCSD/6-311+G(2d,p), QCISD/6-311+G(2d,p), and MP4(SDQ)/6-311+G(2d,p) levels of theory yield for C_8H^- an interesting polyyne-type structure that defies the chemical formula displaying a simple alternation of triple and single carbon−carbon bonds, $[:C\equiv C-C\equiv C-C\equiv C-C\equiv CH]^{1-}$. In the optimized geometry of C_8H^-, as one proceeds from the naked carbon atom on one side of the chain to the CH unit on the opposite side of the chain, the short (formally triple) carbon−carbon bonds *decrease* in length from 1.255 to 1.213 Å whereas the long (formally single) carbon−carbon bonds *increase* (albeit only slightly) in length from 1.362 to 1.378 Å (CCSD results). In striking contrast, both MP2 and DFT (B3LYP and PBE0) calculations fail in reproducing the pattern of the carbon−carbon bond lengths obtained with the CCSD, QCISD, and MP4 methods. The structures of three shorter *n*-even chains, C_nH^- ($n = 2$, 4, and 6), along with those of four *n*-odd compounds ($n = 3$, 5, 7, and 9) are also investigated at the CCSD/6-311+G(2d,p) level of theory.

1. Introduction

The present theoretical study is motivated by the recent discovery of octatetranyl anion, C_8H^-, independently made by two groups of astrophysicists.[1,2] Brünken et al.[1] have detected C_8H^- in the dark cloud TMC-1 and Remijan et al.[2] have detected it in the circumstellar envelope IRC +10216. The positive identification of this linear carbon chain anion was aided by an early laboratory study concerned with the characterization of its rotational spectrum.[3] Because shorter carbon chain anions with closed-shell electronic structures and general formula C_nH^- ($n = 4$ and 6) have already been detected in different astronomical environments,[4,5] an interesting question arises as to what is the longest chain carbon anion that may be present in the interstellar medium (ISM). Besides its significance within the context of astrochemistry,[6] the molecular structure of C_8H^- poses a number of interesting questions to physical and theoretical chemists as well: can its structure be described with a chemical formula showing alternate triple and single bonds, as shown below? What are the lengths of its carbon−carbon bonds? Is the negative charge localized on the terminal carbon atom or distributed throughout the entire polyyne chain? Answers to these questions can hopefully be obtained from the results of electronic structure theory calculations which, together with laboratory experiments, represent an invaluable tool for the characterization of exotic carbon clusters and molecules.[7,8]

$$[:C_1\equiv C_2–C_3\equiv C_4–C_5\equiv C_6–C_7\equiv C_8-H]^{1-}$$

In this study we employ both ab initio post-Hartree−Fock (post-HF) and density functional theory (DFT) methods[9–11] to characterize the geometry of C_8H^- in its ground electronic state. The accurate quantum mechanical treatment of the C_8H^- anion is quite challenging because the following considerations need to be taken into account. First, the molecule contains 16 π-electrons associated to four (formally) triple bonds connected to each other through three (formally) single bonds. Hence, because π-electron conjugation is expected to be operative in this molecule, a single determinant description may be inaccurate thus requiring the use of multiconfigurational wave functions such as those obtained from the complete active space self-consistent field (CASSCF) method.[12] In this case, however, besides selecting the correct active space, one faces the serious problem of the active space size, which in most quantum chemistry codes is limited to about 15 orbitals.[12] Among the single-reference based post-HF methods, coupled-cluster theory[13] appears to be a reasonable choice for the quantum mechanical treatment of a closed-shell species such as C_8H^-. For instance, Botschwina has pioneered the theoretical study of carbon chain clusters and other astrophysically relevant molecules using coupled-cluster theory.[14,15] Second, the molecule is negatively charged, meaning that diffuse functions are to be included into the basis set. Extended basis sets are therefore necessary to accurately determine the geometry of C_8H^-, but the size of this molecular anion foresees the need for very large computational resources particularly if one wants to use highly correlated post-HF methods. The choice of the method/basis-set combination (or model chemistry) thus needs to proper balance the above requirements. Furthermore, a series of benchmark calculations are necessary so as to validate the theoretical approach adopted in the study of polyyne carbon chains.

So far, and to the best of our knowledge, few computational studies have been carried out on the octatetranyl anion. In 2003 Pan et al.[16] performed a density functional theory (DFT) study of C_nH^- ($n \leq 10$) clusters at the B3LYP/6-311G(d,p) level of theory. Interestingly, they found that the geometries of the

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anionic clusters are linear up to $n = 9$ whereas $C_{10}H^-$ has been predicted to have a cyclic structure. For C_8H^- these authors predicted a linear structure with the shortest (formally) single bond connecting C_4 to C_5 and the shortest (formally) triple carbon−carbon bond located near the terminal hydrogen atom. More recently, Gupta et al.[3] have computed the rotational constant of C_8H^- at the CCSD(T)/cc-pVTZ level and the vibration−rotation correction at the SCF/DZP level. However, the computed geometric parameters of C_8H^- were not discussed in their astrophysically oriented study. Further, because the basis sets employed in these studies did not include diffuse functions, which are necessary for the accurate quantum mechanical modeling of closed-shell anions,[10] it is interesting to know what level of theory is the most appropriate and, at the same time, computationally affordable to correctly predict the equilibrium molecular structure of the octatetranyl anion.[17] For the sake of comparison, we investigate also the equilibrium structures of three shorter n-even carbon chains, C_nH^- ($n = 2$, 4, and 6), along with those of four n-odd compounds ($n = 3$, 5, 7, and 9). As a note of general interest, the parent neutral (open-shell) radical C_8H has already been detected both in the circumstellar envelope IRC +10216[18] and in the dark cloud TMC-1[19] as well as characterized in the laboratory.[20] On the other hand, the molecular cation C_8H^+ has been experimentally and theoretically investigated by Maier and co-workers[21] but, to the best of our knowledge, its presence in the ISM has not been revealed yet.

2. Methods and Benchmark Calculations

As for the reference molecule of our benchmark calculations, we chose acetylene (HC≡CH), for which accurate bond lengths have been experimentally determined by Baldacci et al.[22] using rotational spectroscopy. From the rotational spectra of three isotopic molecules ($^{12}C_2H_2$, $^{12}C_2D_2$, and $^{12}C_2HD$) these authors have determined the equilibrium internuclear distances of acetylene being $r_e(C-H) = 1.06215 \pm 17 \times 10^{-5}$ Å and $r_e(C\equiv C) = 1.20257 \pm 9 \times 10^{-5}$ Å. Geometry optimization of the acetylene molecule in the electronic ground state ($X\ ^1\Sigma_g^+$) was performed at the ab initio post-HF level using the coupled-cluster (CC) method with single and double substitutions,[13] hereafter referred to as CCSD, with the quadratic configuration-interaction method including single and double substitutions (QCISD),[23] and with the second- and fourth-order Møller−Plesset (MP) perturbation theory methods[24] referred to as MP2 and MP4, respectively. For the latter in particular, the single, double, and quadruple substitutions were employed, which is denoted to as MP4(SDQ).[25,26] Further, and for the sake of comparison, the popular B3LYP hybrid functional of Becke[27–29] and the PBE0 (also known as PBE1PBE) hybrid functional of Adamo, Barone, and Scuseria[30,31] were also employed in this study. Two groups of basis sets were employed in conjunction with all of the above methods. The first group includes the standard 6-31+G(2d,p) and the 6-311+G(2d,p) basis sets of Pople and co-workers.[32–34] Both basis sets are provided with polarization functions (i.e., two sets of d-type functions for carbon and one set of p-type functions for hydrogen) along with diffuse functions (on carbon only), which are necessary for the quantum mechanical description of molecular anions.[10] Pure d-type functions were employed for these basis sets. The second group comprises Dunning's correlation consistent basis sets[35] cc-pVDZ, cc-pVTZ, and aug-cc-pVDZ, the latter of which contains diffuse functions.

TABLE 1: Computed Bond Lengths (Å), Chain Length (Å), Dipole Moment (Debye), and Equilibrium Rotational Constant (MHz) of C_8H^-

parameter	CCSD[a]	QCISD[a]	MP4(SDQ)[a]	MP2[a]	B3LYP[b]	PBE0[b]
C_1-C_2	1.255	1.257	1.257	1.274	1.265	1.265
C_2-C_3	1.362	1.362	1.362	1.341	1.341	1.341
C_3-C_4	1.230	1.231	1.230	1.254	1.245	1.243
C_4-C_5	1.364	1.364	1.365	1.337	1.339	1.339
C_5-C_6	1.222	1.223	1.223	1.247	1.239	1.237
C_6-C_7	1.378	1.378	1.378	1.355	1.354	1.354
C_7-C_8	1.213	1.214	1.214	1.231	1.225	1.223
C_8-H	1.065	1.065	1.065	1.064	1.063	1.065
C_1/H	10.089	10.094	10.094	10.103	10.071	10.066
μ	13.7	13.7	13.7	12.2	10.6	10.8
B_e	577.0	576.5	576.4	576.7	580.2	581.1

[a] In combination with the 6-311+G(2d,p) basis set. [b] In combination with the 6-31+G(2d,p) basis set.

The results of our benchmark calculations on acetylene are reported in Table 1S (see Supporting Information). The bond lengths of acetylene computed at the CCSD/6-311+G(2d,p) level of theory are in remarkable agreement with the experimental values, closely followed by those computed at the MP4(SDQ)/6-311+G(2d,p) and QCISD/6-311+G(2d,p) levels of theory. When the Dunning's double-ζ basis-set (cc-pVDZ) with or without diffuse functions is used in conjunction with the CCSD method, the carbon−carbon bond length of acetylene becomes slightly lengthened by ~0.02 Å whereas the C−H bond length lengthens by ~0.01 Å. Only with the more expensive cc-pVTZ basis set,[36] however, is it possible to obtain an almost perfect agreement between computed and experimental bond lengths being $r_e(C\equiv C) = 1.203$ Å and $r_e(C-H) = 1.062$ Å. The bond lengthening effect observed upon changing the type of basis set (i.e., from Pople-type to Dunning-type double-ζ) occurs also when the MP2 method is employed though the carbon−carbon bond length computed at the MP2/6-311+G(2d,p) level of theory is somewhat stretched (1.211 Å) with respect to the experimental value. As for the hybrid DFT methods, B3LYP and PBE0, the bond lengths that are closer to experiment are those computed with the 6-31+G(2d,p) basis set whereas the larger 6-311+G(2d,p) basis set yields bond lengths that are slightly shorter than those experimentally determined by Baldacci et al.[22]

From the results of our benchmark calculations performed on molecular acetylene, and taking into account the computational resources necessary to treat the larger octatetranyl anion, the following method/basis set combinations were selected for the quantum chemical study of C_8H^-: CCSD/6-311+G(2d,p), QCISD/6-311+G(2d,p), MP4(SDQ)/6-311+G(2d,p), MP2/6-311+G(2d,p), B3LYP/6-31+G(2d,p) and PBE0/6-31+G(2d,p). All the quantum chemical calculations were performed with the parallel version of the Gaussian 03 software package.[37] Pre- and postprocessing operations were carried out with the GaussView (4.1)[38] and Molden (4.6)[39] graphic software interfaces.

3. Results and Discussion

3.1. Geometries. Table 1 reports the results of our ab initio post-HF and DFT calculations performed on the octatetranyl anion in the electronic ground state ($X\ ^1\Sigma^+$). The bond lengths computed at the CCSD/6-311+G(2d,p), QCISD/6-311+G(2d,p), and MP4(SDQ)/6-311+G(2d,p) levels of theory are in excellent agreement with each other. They indicate that the linear carbon chain ($C_{\infty v}$) is characterized by an alternation of short and long carbon−carbon bonds. Interestingly, however, we notice that the short carbon−carbon bonds computed with the CCSD method are not equivalent for they *shorten* on going from C_1-C_2 (1.255 Å) to C_7-C_8 (1.213 Å). The latter bond length is close to the canonical triple bond of acetylene at 1.203 Å (see Table 1S). On the other hand, the long carbon−carbon bonds of C_8H^-

TABLE 2: Chain Length (Å), Dipole Moment (Debye), Equilibrium Rotational Constant (GHz), HOMO−LUMO Energy Gap (eV), and the Singlet−Triplet Energy Separation (kcal mol^{-1}) of C_nH^- (n = 2−9) As Computed at the (U)CCSD/6-311+G(2d,p) Level of Theory

parameter	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$
C_1/H	2.318	3.674	4.917	6.235	7.504	8.803	10.089	11.372
μ	3.6	4.8	6.7	7.2	10.1	10.0	13.7	13.0
B_e	41.798	10.915	4.623	2.348	1.364	0.861	0.577	0.407
H−L	9.04	7.67	8.14	7.72	7.86	7.72	7.68	7.66
ΔE_{S-T} [a]	102.1	−14.8	90.7	−19.7	65.4	−17.0	64.2	−14.9

[a] Positive values indicate a ground-state singlet.

slightly *increase* in length on going from C_2-C_3 (1.362 Å) to C_6-C_7 (1.378 Å). In comparison, the canonical single C−C bond of ethane and the canonical double C=C bond of ethylene computed at the CCSD/6-311+G(2d,p) level of theory have a length of 1.530 and 1.334 Å, respectively. It follows that the long carbon−carbon bonds in C_8H^- are closer to elongated double bonds rather than shortened single bonds and, hence, the chemical formula shown above is completely unrealistic. Further, the reason for the observed asymmetry in the carbon−carbon bond lengths of C_8H^- is due to the terminal H atom which breaks the symmetry plane perpendicular to the molecular axis. This symmetry plane is, however, present in both HC_8H and C_8^{2-} ($D_{\infty h}$) where the carbon−carbon bond lengths are symmetric with respect to the corresponding chain centers.

Both hybrid DFT functionals reproduce fairly well the trend described above as far as the short carbon−carbon bonds are concerned whereas this is not the case for the long carbon−carbon bonds. As seen in Table 1, C_4-C_5 (1.339 Å) is slightly *shorter* than C_2-C_3 (1.341 Å) at both the B3LYP/6-31+G(2d,p) and PBE0/6-31+G(2d,p) levels of theory. The same trend is obtained also with the larger 6-311+G(2d,p) basis set (see Table 2S in Supporting Information). Furthermore, it appears that the long (formally single) carbon−carbon bonds computed with these hybrid DFT methods are somewhat shorter with respect to those computed with the CCSD, QCISD, and MP4(SDQ) methods. As a result, the DFT-optimized chain lengths (see parameter C_1/H in Table 1) are ∼0.02 Å shorter than those obtained with the correlated post-HF methods. The chain shortening effect increases to ∼0.07 Å if one uses the larger 6-311+G(2d,p) basis set (see Table 2S in Supporting Information). The worse bond lengths are those obtained at the MP2/6-311+G(2d,p) level of theory where the (formal) triple bonds are too much elongated whereas the (formal) single bonds are significantly compressed with respect to the CCSD results. As a result, the MP2 geometry has the larger chain length of all (C_1/H = 10.103 Å). More upsetting, however, is the fact that like DFT also the MP2 model produces the wrong trend in the long carbon−carbon bonds of C_8H^- with C_4-C_5 (1.337 Å) being slightly *shorter* than C_2-C_3 (1.341 Å), as shown in Table 1. These results call for a revision of the molecular structure of C_8H^- predicted by Pan et al.[16]

3.2. Properties. The structural problems highlighted above are likely to have serious consequences for the prediction of the gas-phase physicochemical properties of C_8H^- computed with the popular DFT and MP2 methods in combination with commonly used basis sets. In the following part we will discuss in detail the dipole moment, equilibrium rotational constant, frontier orbitals, and charge distribution of the octatetranyl anion.

3.2.1. Dipole Moment. The magnitude of the dipole moment computed with the CCSD, QCISD, and MP4(SDQ) methods corresponds to 13.7 Debye, as reported in Table 1. In comparison, the value of μ computed at the MP2/6-311+G(2d,p) level of theory is slightly smaller, being 12.2 Debye, whereas the dipole moments computed with the B3LYP (10.6 Debye) and PBE0 (10.8 Debye) methods are ∼3 Debye smaller than the CCSD value. The only value of μ that is available for comparison is that of 11.9 Debye computed by Gupta et al.[3] at the CCSD(T)/cc-pVTZ level of theory. We notice, however, that the absence of diffuse functions (included with the prefix "aug") in the latter basis set might result in possible errors in the electronic energy and molecular properties.[10] In summary, it appears that our CCSD result yields an upper bound for the dipole moment of C_8H^- whereas B3LYP produces a lower bound for it.

3.2.2. Rotational Constant. At the bottom of Table 1 is also reported the equilibrium rotational constant B_e of the octatetranyl anion which corresponds to 577.0 MHz as computed at the CCSD/6-311+G(2d,p) level of theory (in comparison, the value of B_e computed for HC_8H corresponds to 559.6 MHz). The values of B_e obtained with both the QCISD and MP4(SDQ) methods are very close in magnitude, being 576.5 and 576.4 MHz, respectively, whereas the MP2 value of B_e is 576.7 MHz. Both DFT methods give higher B_e values of 580.2 (B3LYP) and 581.1 (PBE0) MHz. Gupta et al.[3] reported a value of B_e = 583.2 as computed at the CCSD(T)/cc-pVTZ level of theory, which is in excellent agreement with their experimental value of 583.34014(8) MHz obtained from the rotational spectrum. We notice, however, that calculations performed by Sherrill et al.[40] indicate that the C≡C bond of acetylene optimized at this level of theory (1.210 Å) is slightly lengthened with respect to experiment (see Table 1S in Supporting Information). We confirmed this computational result by optimizing the geometry of acetylene at the CCSD(T)/cc-pVTZ level using numerical gradients (analytical gradients for the CCSD(T) method were not available). Hence, considering the accuracy attained for the geometrical parameters of the reference molecule and the absence of diffuse functions in the cc-pVTZ basis set necessary to describe anionic states, it is difficult to reconcile the excellent experimental agreement of the computed rotational constant of C_8H^- obtained by Gupta and co-workers.[3]

Also, these authors computed a vibration−rotation correction of 3.5 MHz at the noncorrelated SCF/DZP level.[3] Owing to the very large computational cost associated to the calculation of anharmonic frequencies and anharmonic zero-point energies (ZPEs) using correlated methods, we are unable to estimate the vibration−rotation correction at the CCSD/6-311+G(2d,p) level and refrain from computing it using a noncorrelated ab initio method. This state of affairs precludes us from obtaining a vibrationally averaged structure (at 0 K), which includes the effects of molecular vibrations and anharmonicity on the equilibrium geometry.[41,42] However, we did calculate the harmonic normal modes of vibration at the CCSD/6-311+G(2d,p) level with both analytical and numerical gradients so as to estimate the (harmonic) ZPE of the octatetranyl anion. Our results indicate that the harmonic ZPE of C_8H^- (25.23 kcal/mol) is about three times larger than that of C_2H^- (8.88 kcal/mol).

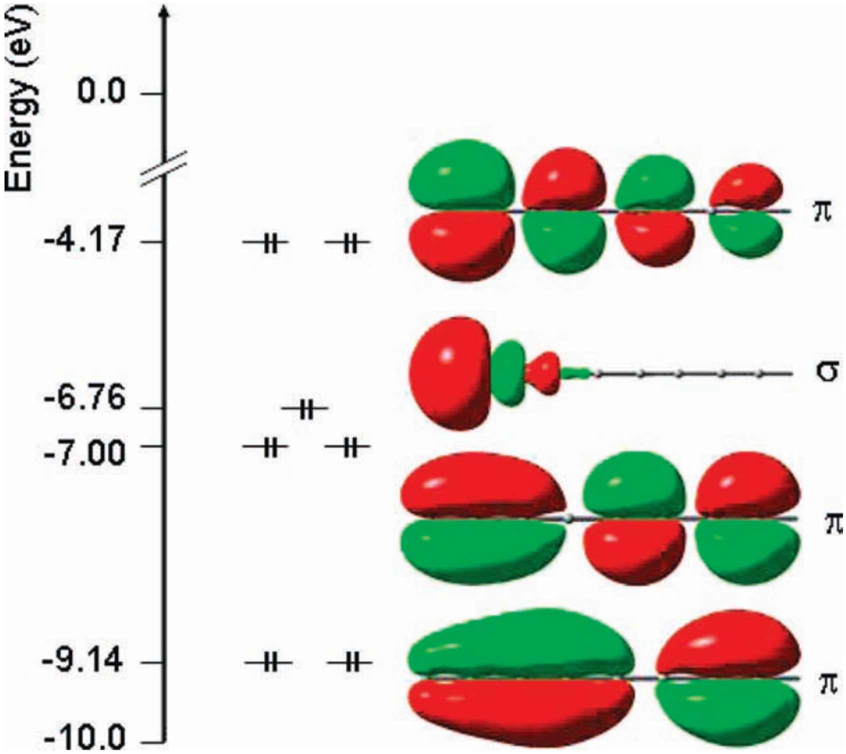

Figure 1. Frontier orbitals of C_8H^- in the energy range from 0 to −10 eV.

3.2.3. Frontier Orbitals. Figure 1 shows the energy diagram and plots of the frontier orbitals of C_8H^- in the energy range from 0 to −10 eV, as computed at the CCSD/6-311+G(2d,p) level of theory. The highest-occupied molecular orbital (HOMO) possesses π-type symmetry and is doubly degenerate with four p_π electrons. The HOMO−1 is ~2.6 eV lower in energy and as shown in the figure it possesses σ-type symmetry and is semilocalized on one side of the molecule. We notice that this MO, which bears the lone-pair on the naked carbon atom, has a strong similarity with the HOMO−2 of phenyl-acetylide anion.[43] Just ~0.2 eV below HOMO−1 is the HOMO−2, which is doubly degenerate and possesses π-type symmetry. In contrast to HOMO, which is characterized by three nodes, the HOMO−2 has two nodes (one of which is located near C_4) whereas HOMO−3, also doubly degenerate, possesses only one node bisecting the C_5−C_6 bond. Thus, the topology of HOMO is in line with the trend in the short/long carbon−carbon bond lengths discussed above albeit the nonsymmetric distribution of the π-electrons in the chain is responsible for the different degree of shortening and lengthening of the carbon−carbon bonds (Table 1). Finally, it is worth noticing that the lowest-unoccupied MO (LUMO) of C_8H^- possesses σ-type symmetry (not shown) and the HOMO−LUMO energy gap computed at the CCSD/6-311+G(2d,p) level of theory corresponds to 7.68 eV which is ~2.8 eV lower than that computed at the same level for HC_8H (10.51 eV).

3.2.4. Charge Distribution. The Mulliken atomic charges computed at the CCSD/6-311+G(2d,p) level of theory indicate that the most negatively charged atom among those of C_8H^- is C_1 (−1.37) followed by C_8 (−1.18). The charges of the remaining atoms are as follows: C_2 (1.04), C_3 (−0.69), C_4 (0.13), C_5 (0.56), C_6 (−0.97), C_7 (1.34), and H (0.14). Despite the well-known shortcomings of the Mulliken population analysis,[10] its results appear in line with the topology of the σ-type frontier orbital HOMO−1 depicted in Figure 1 which assigns the lone-pair to the naked carbon atom. We also performed a natural population analysis (NPA)[44] of the CCSD density but the noninteger value of the total natural charge (−0.92673) computed at this level of theory prevented us from discussing further on this issue.

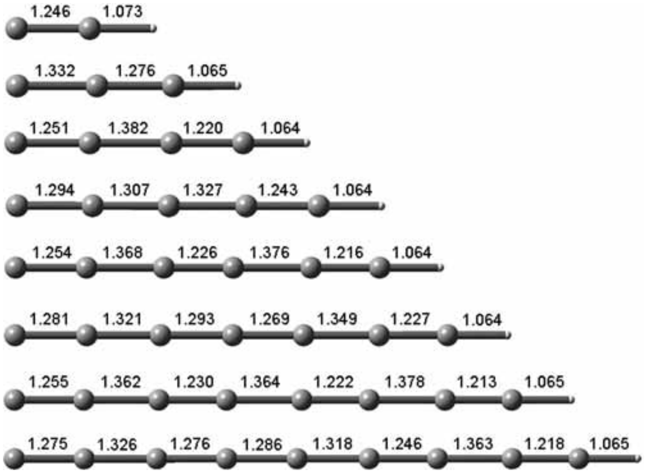

Figure 2. Bond lengths of C_nH^- ($n = 2-9$) optimized at the (U)CCSD/6-311+G(2d,p) level of theory.

3.3. C_nH^- Anions (n = 2−9). As mentioned in the Introduction, shorter carbon chain anions containing four and six carbon atoms and characterized by a closed-shell electronic structure have also been identified in the ISM.[4,5] It is therefore interesting to compare the optimized structure of C_8H^- with those of C_nH^- (n = 2, 4, and 6). For the sake of comparison, we also include four compounds containing an odd number of carbon atoms, namely n = 3, 5, 7, and 9 which have been recently considered in a chemical model of carbon-rich astronomical environments.[6] The bond lengths of the eight carbon chain anions optimized at the (U)CCSD/6-311+G(2d,p) level of theory are shown in Figure 2. Let us first analyze the equilibrium geometries of the n-even compounds. Interestingly, like in C_8H^- also in C_6H^- the short carbon−carbon bond distances shorten from 1.254 Å (C_1−C_2) to 1.216 Å (C_5−C_6)

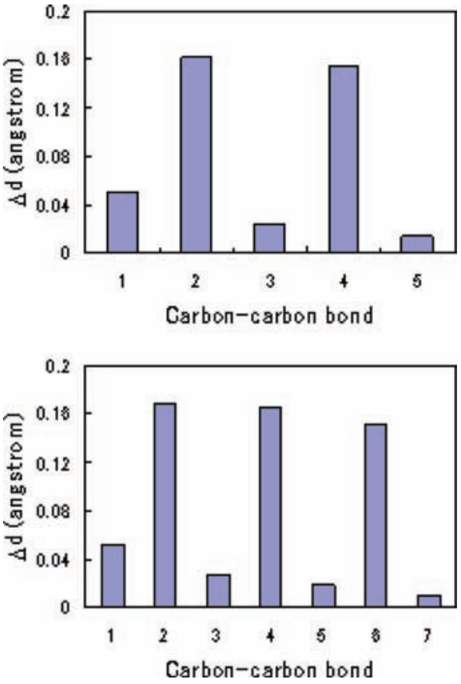

Figure 3. Deviation of the longer *n*-even carbon chains C_6H^- (top) and C_8H^- (bottom) from an ideal polyyne-type structure.

whereas the long carbon−carbon bonds slightly elongate from 1.368 Å (C_2-C_3) to 1.376 (C_4-C_5) Å. In C_4H^- the short carbon−carbon bond distances shorten from 1.251 Å (C_1-C_2) to 1.220 Å (C_3-C_4) whereas the central carbon−carbon bond is at 1.382 Å. The carbon−carbon bond of C_2H^- is at 1.246 Å whereas the C−H bond is at 1.073 Å. Hence, removal of H^+ from molecular acetylene (Table 1S) yields an anion with an *elongated* carbon−carbon bond whereas the elongation of the C−H bond is minimal. As far as the longer *n*-even ($n = 6, 8$) chains are concerned, taking as reference the carbon−carbon bond lengths of acetylene (1.203 Å) and ethane (1.530 Å), it is observed from Figure 3 that the deviation from an ideal polyyne-type structure made of alternate single and triple bonds arises mainly from the (formally) single carbon−carbon bonds. These bonds appear to be considerably shorter than a canonical single carbon−carbon bond as a result of the π-conjugation that operates throughout the chain.

We notice that the DFT-optimized structures obtained by Pan et al.[16] display the correct trend in both the short and long carbon−carbon bond lengths for chains up to C_6H^- but this is not the case for C_8H^- where the shortest (formally) single carbon−carbon bond is located on the central C_4-C_5 unit as in our DFT-optimized structures (Table 1). Thus, the structure of C_8H^- predicted by Pan et al.[16] should be revised to that shown in Figure 2. Similar structural problems with the lengths of conjugated carbon−carbon bonds optimized with popular DFT methods were encountered by the author in a recent theoretical study of the phenyl-acetylide anion.[43] It is likely that these structural problems are being related to the overstabilization of conjugated cumulenes over polyynes by the most popular DFT methods, as thoroughly discussed by Woodcock et al.[45] One possible way to overcome them is through the development of a new generation of density functionals.[46]

Let us now analyze the equilibrium geometries of the *n*-odd compounds. In this group, the lowest-energy structures are those corresponding to the triplet ground state ($X\ ^3\Sigma^-$) as indicated by the singlet−triplet energy separation (ΔE_{S-T})[47] reported at the bottom of Table 2. We notice that the shortest carbon−carbon bond in each chain is the one connected to the terminal hydrogen atom whereas the neighboring carbon−carbon bond is always the longest one. The longer *n*-odd chains ($n = 7, 9$) deviate from an ideal cumulene-type structure made of consecutive double bonds of equal length. As shown in Figure 2, only two consecutive carbon−carbon bonds in the $C_3-C_4-C_5$ moieties of C_7H^- and C_9H^- are characterized by similar lengths. The trends in the carbon−carbon bond lengths of C_9H^- and C_7H^- qualitatively agree with those computed by Pan et al.[16] using DFT whereas this is not the case for C_5H^-. Accordingly, our CCSD results shown in Figure 2 indicate that the C_2-C_3 bond of C_5H^- is *shorter* than C_3-C_4 whereas DFT indicates them having an equal length of 1.31 Å (see Figure 7 in ref 16).

Table 2 compares the computed CCSD values of the chain length, dipole moment, equilibrium rotational constant, HOMO−LUMO energy gap, and the singlet−triplet energy separation (ΔE_{S-T}) of the C_nH^- ($n = 2-9$) specie. The dipole moment of the *n*-even anions increases with chain length, being 3.6 D (C_2H^-), 6.7 D (C_4H^-), 10.1 D (C_6H^-), and 13.7 D (C_8H^-). This trend in the magnitude of μ can be rationalized by considering the increase in Mulliken atomic charge of the naked carbon atom (C_1) which corresponds to −0.80 (C_2H^-), −1.05 (C_4H^-), −1.17 (C_6H^-), and −1.37 (C_8H^-). Also the dipole moment of the *n*-odd anions increases with chain length, being 4.8 D (C_3H^-), 7.2 D (C_5H^-), 10.0 D (C_7H^-), and 13.0 D (C_9H^-). The rotational constant of the anions decreases about 1 order of magnitude, from 41.798 GHz (C_2H^-) to 0.407 GHz (C_9H^-), upon increasing the length of the carbon chain. The HOMO−LUMO gap of the *n*-even compounds decreases with chain length from 9.04 eV (C_2H^-) to 7.68 eV (C_8H^-) whereas that of the *n*-odd anions remains nearly constant at about 7.7 eV. The decrease in the HOMO−LUMO gap as a function of increasing chain length for the *n*-even compounds parallels the decrease in the energy associated to the stepwise addition of C_2 units to C_2H^-, which can be calculated from the following equation:

$$\Delta E_{n,n+2} = [E(C_nH^-) - E(C_{n+2}H^-)]$$

where $E(C_nH^-)$ and $E(C_{n+2}H^-)$ are the total electronic energies of the carbon chain anions that differ by two carbon atoms.[48] This relationship between the HOMO−LUMO gap and $\Delta E_{n,n+2}$, however, does not hold for the *n*-odd compounds. This difference is likely to arise from the different spin multiplicity of the electronic ground states of these *n*-even (singlet) and *n*-odd (triplet) carbon chain anions.

4. Conclusions

In this study we investigated the ground-state equilibrium geometry and electronic structure of the octatetranyl anion recently detected in the ISM with the aid of both post-HF and DFT methods. The model chemistry employed here is based on extensive benchmark calculations performed on the acetylene molecule whose gas-phase structure has been experimentally characterized with high accuracy. It appears that the MP2 method as well as the B3LYP and PBE0 hybrid functionals are unable to reproduce the trend in the carbon−carbon bond lengths of C_8H^- obtained with the CCSD, QCISD, and MP4(SDQ) methods. This state of affairs is rather surprising given that the structural problems discussed herein are concerned with the ground-state electronic structure of a closed-shell anion containing only carbon and hydrogen atoms. Although, on the one hand, this study indicates that extreme care should be exercised in predicting the gas-phase equilibrium structures and spectroscopic properties of unsaturated carbon cluster anions computed with the most popular DFT methods, on the other hand, it hopes to provide further ground for the improvement and development of modern exchange-correlation functionals.

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Supporting Information Available: Tables containing the results of our benchmark calculations on molecular acetylene and additional DFT results on the octatetranyl anion. This material is available free of charge via the Internet at http://pubs.acs.org.

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