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π Electron Delocalization and Compression in Acyclic Acetylenic Precursors to Multidimensional Carbon Networks: Comparison with Experiment for the Recently Synthesized Tris(trimethylsilyl)-Substituted Tetraethynylmethane. Structures, Thermochemistry, Infrared Spectra, Polarizabilities, and Hyperpolarizabilities

Buyong Ma, Horst M. Sulzbach, Yaoming Xie, and Henry F. Schaefer III*

Contribution from the Center for Computational Quantum Chemistry, The University of Georgia, Athens, Georgia 30602

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Abstract: Several acyclic acetylenic precursors to multidimensional carbon networks, including tetraethynylbutatriene ($C_{12}H_4$), tetraethynylmethane (C_9H_4) derivatives, and the yet unknown molecules tetraethynylallene ($C_{11}H_4$) and hexaethynyl[3]radialene ($C_{18}H_6$), have been studied using *ab initio* molecular quantum mechanics. Their equilibrium geometries, vibrational frequencies, thermochemical properties, and nonlinear optical responses have been predicted. To allow direct comparisons with experiment, the recently synthesized tris(trimethylsilyl)tetraethynylmethane molecule was also studied quantum mechanically. Excellent agreement with the experimental geometry and vibrational frequencies for the tetraethynylbutatriene ($C_{12}H_4$) molecule has been achieved. However, the C≡C bond contraction, which was found by X-ray diffraction in the tris(trimethylsilyl)tetraethynylmethane crystal, is not reproduced by our research. We suggest that a novel mechanism, which we call "π electron compression", might be responsible for part of the deviation of the X-ray structure from our theoretical results. Therefore, it may be advisable to reexamine the structure by both X-ray and neutron diffraction. The π electron compression effects have been employed to explain the negative nonadditivity of the (hyper)polarizability of the C_9H_4 molecule and the effects of the substitution of hydrogen atoms by lithium atoms, fluorine atoms, cyano groups, and acetylenic groups. The HOMO energy and nonadditivity of the (hyper)polarizability for the $C_{11}H_4$ molecule are lower than those for other planar molecules. The heats of formation for the precursors are evaluated. They are 236, 247, 289, 317, and 437 kcal mol^{-1} for the C_9H_4, $C_{10}H_4$, $C_{11}H_4$, $C_{12}H_4$, and $C_{18}H_6$ molecules, respectively. The heat of formation of the tris(trimethylsilyl)tetraethynylmethane decreases to 76 kcal mol^{-1}, partially due to the hyperconjugation effect of the TMS groups.

1. Introduction

Recently, the preparation of polymeric network allotropes of carbon has become the subject of much interest.[1-4] The new carbon network compounds may exhibit unusual properties, such as hardness, thermal and electrical conductivity, and lubrication,[1,3,4] in part due to through-space and through-bond interaction. The design, preparation, and study of novel molecular and polymeric allotropic forms of carbon will likely be a central topic in chemistry in the coming decades.[1] The key step in preparing such networks may be the synthesis of monomeric precursors with a high C:H ratio. Acyclic acetylenic precursors are obvious possibilities in this respect.

The synthesis of these monomeric precursors has proven to be both challenging and encouraging.[1,3-5] The synthesis of a substituted tetraethynylmethane (C_9H_4) succeeded very recently, after a lengthy search and several unsuccessful attempts.[6] Tetraethynylethylene ($C_{10}H_4$)[1b] was elusive until 1991. A similarly recalcitrant compound, tetraethynylallene ($C_{11}H_4$) is yet unknown. It was recently reported[7] that tetraethynylbutatriene ($C_{12}H_4$) has been synthesized. Hexaethynyl[3]radialene ($C_{18}H_6$) is another such target compound. There are at least two attractive $C_{18}H_6$ isomers, the first being 1,7,13-cyclooctadecatriene-3,5,9,11,15,17-hexayne and the second hexaethynylbenzene.[3b] Hexaethynyl[3]radialene[1,8] ($C_{18}H_6$) may in time be prepared following the radialene synthesis starting from 1,1-dibromoolefins. However, there has been no reported research along these lines to date.

The very recent synthesis[6] of a substituted tetraethynylmethane is very important. It allows a comparison between theoretical and experimental results for this important molecule. Tetraethynylmethane is the archetypal high carbon content monomer whose polymerization can, in principle, lead to a three-dimensional carbon network homologous to diamond.[1] Besides its potential usage as the precursor, the tetraethynylmethane provides an interesting bonding pattern, since four alkynyl units are bonded to a single carbon atom. The X-ray analysis[6] for the tris(trimethylsilyl)-protected species revealed some interesting features. The most striking one is a large alkynyl bond contraction in the tris(trimethylsilyl)-protected tetraethynylmethane (1.14 and 1.16 Å compared to 1.20 Å for acetylene).[6] It is of

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fundamental importance to know whether the reported value is incorrect or if a novel contraction mechanism is operative.

Acyclic acetylenic precursors themselves have interesting physical organic properties, mainly due to their cross-conjugation and geminal alkynyl groups.[1-5] An understanding of the possible interaction between the geminal alkynyl groups is very important, not only for the precursors themselves but also for the polymeric networks. All such compounds synthesized so far are unstable at room temperature.[1-8] The heats of formation of those molecules should be very high, and this may be one of the reasons for their instability. Other potentially important properties, expected for these highly conjugated system, are their (hyper)polarizabilities. The evaluation of the (hyper)polarizabilities for these precursors, which have different combinations and orientations of acetylenic groups, will provide important information about the structure–properties relationship for this kind of molecule, especially with respect to the π electron interaction.

In this paper, we present the results of our theoretical studies for several important acyclic acetylenic precursors, including the tetraethynylmethane (C_9H_4) derivatives, tetraethynylethylene ($C_{10}H_4$), tetraethynylallene ($C_{11}H_4$), tetraethynylbutatriene ($C_{12}H_4$), and hexaethynyl[3]radialene ($C_{18}H_6$) molecules, with emphasis on the tetraethynylmethane derivatives. It is hoped that this research will contribute to a general understanding of these molecules. Our structural and vibrational frequency information for those molecules may be helpful for the identification of the new compounds ($C_{11}H_4$ and $C_{18}H_6$).

In the present publication, the formulae C_9H_4, $C_{10}H_4$, $C_{11}H_4$, $C_{12}H_4$, and $C_{18}H_6$ refer to tetraethynylmethane, tetraethynylethylene, tetraethynylallene, tetraethynylbutatriene, and hexaethynyl[3]radialene, respectively.

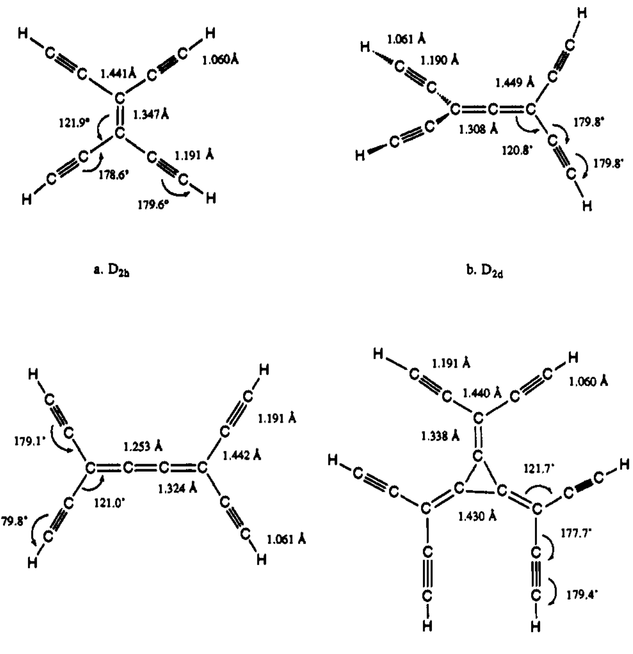
2. Theoretical Approach

The Hartree–Fock or self-consistent-field (SCF) approach has been used to locate stationary points via analytic first derivative techniques. Subsequently, analytical energy second derivative techniques are used to determine the harmonic vibrational frequencies. Correlation energies were evaluated via second-order perturbation theory (MP2) based on the SCF geometries. The basis set adopted for the carbon and hydrogen atoms (double-ζ-plus polarization, DZP) and the methods to obtain IR vibrational frequencies (scaled by 0.9), intensities, and assignment are the same as those in previous work.[9] The basis sets used for fluorine, lithium, and nitrogen atoms are also of DZP quality, with the exponents for the polarization functions being $\alpha_d(F) = 1.0$ and $\alpha_d(N) = 0.8$. For the lithium atom, the technical designation[10a] is Li (8s1p/3s1p), with the p functions used as polarization functions and the orbital exponent being $\alpha_p(Li) = 0.28$. The computations were performed using the exemplary program TURBOMOLE.[11a] The IR intensities were evaluated using the program PSI developed by this research group.[11b] The program CADPAC[11c] was used to optimize the geometry of tetraethynylmethane at the DZP MP2 level.

The energy of a molecule in a static uniform electric field can be expanded as[13]

$$E = E^\circ - \mu_i^\circ F_i - {}^1/_2\alpha_{ij}F_iF_j - {}^1/_6\beta_{ijk}F_iF_jF_k - {}^1/_{24}\gamma_{ijkl}F_iF_jF_kF_l$$

where E° is the unperturbed energy, F_i is the component of the field in the i direction, μ_i° is the permanent dipole moment of the molecules, α_{ij} is the static dipole polarizability tensor, and β_{ijk} and γ_{ijkl} are the first and second dipole hyperpolarizability tensors, respectively. For the centrosymmetric molecules considered in the present research, μ_i° and β_{ijk} vanish. Thus only the α_{ij} and γ_{ijkl} tensors are considered and are evaluated using the program[12] Hondo 8.4. The detailed methodology is described in ref 13. For all studies performed here, the molecular geometries were optimized at the DZP SCF level. However, the evaluation of α_{ij} and γ_{ijkl} tensors requires special basis sets and will be discussed in part C of the Results and Discussion section.



a. D_{2h} b. D_{2d} c. D_{2h} d. D_{3h}

Figure 1. Equilibrium geometries at the DZP SCF level of theory for (a) tetraethynylethene ($C_{10}H_4$); (b) tetraethynylallene ($C_{11}H_4$); (c) tetraethynylbutatriene ($C_{12}H_4$); and (d) hexaethynyl[3]radialene ($C_{18}H_6$).

3. Results and Discussion

A. Molecular Structures and Vibrational Frequencies. (i) Cross-Conjugated Systems Tetraethynylallene ($C_{11}H_4$), Tetraethynylbutatrienes ($C_{12}H_4$), and Hexaethynyl[3]radialene ($C_{18}H_6$). The theoretical equilibrium geometries for tetraethynylallene ($C_{11}H_4$), hexaethynyl[3]radialene ($C_{18}H_6$), and tetraethynylbutatriene ($C_{12}H_4$) are shown in Figure 1. Their theoretical IR vibrational frequencies and their assignments are shown in Figure 2. All three structures are shown from the vibrational frequency analyses to be genuine equilibrium geometries.

Tetraethynylallene has been proposed as the precursor to a three-dimensional allenic carbon network with orthogonal chains.[1] Generally,[14] for an unsubstituted allene, the vibrational frequency of the out-of-phase C=C=C stretch falls between 1900 and 2000 cm^{-1}, and that of the in-phase C=C=C stretch is near 1100 cm^{-1}. These features are roughly reproduced by theory for the yet unknown $C_{11}H_4$, as shown in Figure 2. The agreement for the out-of-phase stretch is very good. However, for the in-phase mode, the theoretical value (scaled, as are all vibrational frequencies reported here, by a factor 0.9 with respect to the DZP SCF results) is 1328 cm^{-1}. Unfortunately, there are no comparable experimental data for the in-phase mode for highly substituted allenes.[14] Moving down in frequency, the C=C=C bending fundamental usually occurs at 356 cm^{-1} in the Raman spectrum with strong intensity.[14] For $C_{11}H_4$, complications arise due to the coupling C=C=C bending and C≡C—C bending. However, the corresponding mode is predicted at 336 cm^{-1} and is both IR and Raman active.

The first tetraethynylcumulene, tetraethynylbutatriene ($C_{12}H_4$), with one more carbon atom than the still unknown tetraethynylallene ($C_{11}H_4$), was synthesized recently.[7] Its X-ray structure

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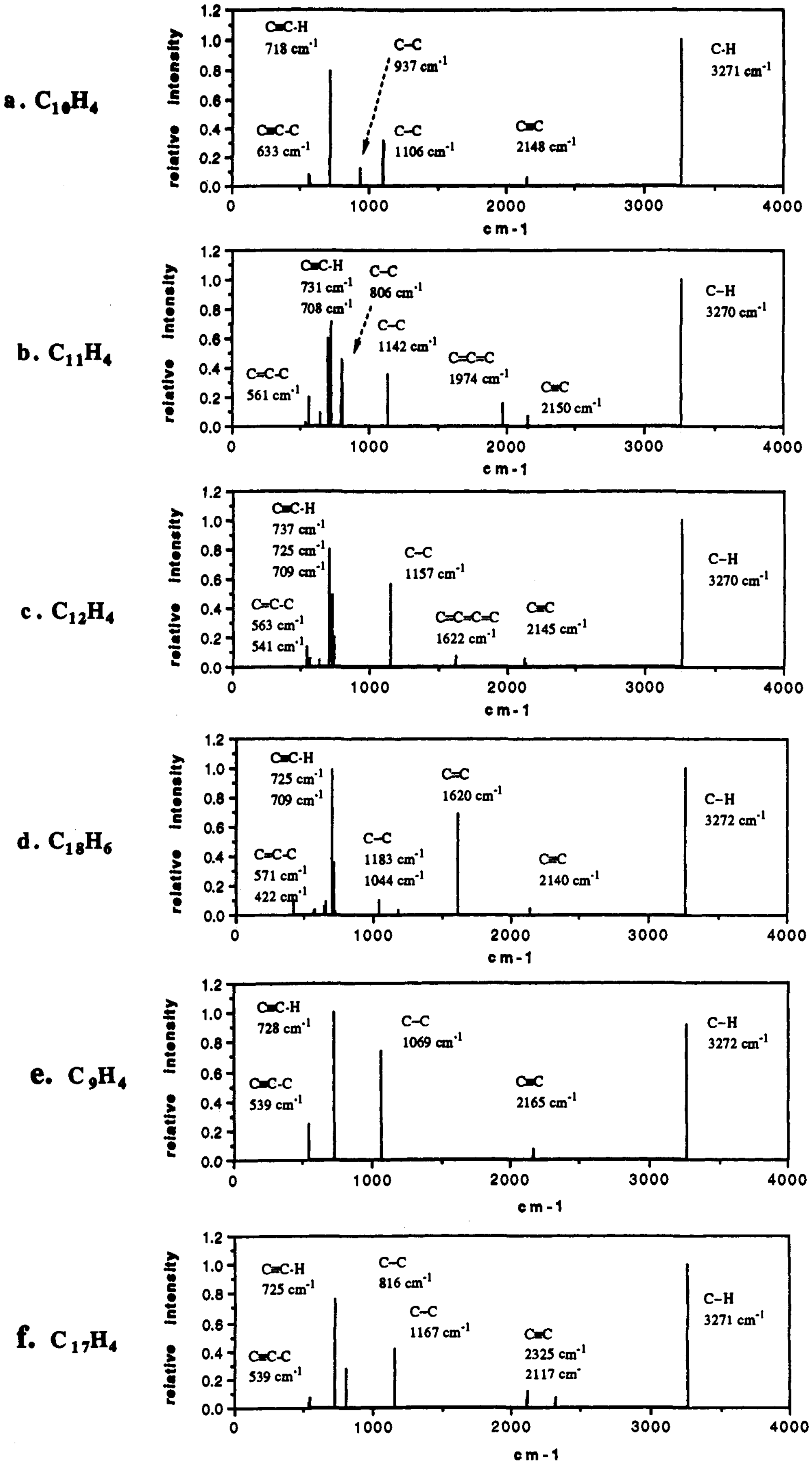

Figure 2. Theoretical IR spectra at the DZP SCF level of theory (scaled by a factor 0.9) for (a) tetraethynylethene ($C_{10}H_4$); (b) tetraethynylallene ($C_{11}H_4$); (c) tetraethynylbutatriene ($C_{12}H_4$); (d) hexaethynyl[3]radialene ($C_{18}H_6$); (e) tetraethynylmethane (C_9H_4); and (f) tetrabutadiynylmethane ($C_{17}H_4$).

shows small deviations from the idea D_{2h} symmetry.[7] However, general agreement between experiment and our theoretical geometry and IR frequencies is achieved, with the central cumulenic C=C bond length agreeing to within 0.005 Å. It was observed that there are two weak IR absorptions at 2144 and 1628 cm^{-1} for C≡C stretch and C=C stretch, respectively, which are in excellent agreement with our theoretical values in Figure 2.

The three molecules, $C_{10}H_4$, $C_{11}H_4$, and $C_{12}H_4$, form a series with increasing cumulenic length. The $C_{10}H_4$ and $C_{12}H_4$ species have planar configurations, and the C—C single bond lengths are almost the same (Figure 1), while the $C_{11}H_4$ molecule has D_{2d} symmetry. It is worth noting that its C—C single bond (1.449 Å) is longer than that in both $C_{10}H_4$ and $C_{12}H_4$ (1.440 Å). One of the reasons for the difference in bond length may be that the π electron conjugation between the acetylenic and the cumulenic groups is less effective in the nonplanar configuration (also see our discussions about thermochemistry and polarizability).

Hexaethynyl[3]radialene is another yet unknown molecule. The most interesting feature of this molecule is the highly strained central three-membered ring. One of the parent compounds of this $C_{18}H_6$ structure is the simple [3]radialene, which is well characterized both experimentally and theoretically.[8] It has been reported that in [3]radialene and its hexamethyl derivative the endocyclic bonds show the expected contraction[8] to approximately 1.453 Å and the exocyclic C=C bond distance is 1.343 Å. Our theoretical results (Figure 1) are in good agreement with the related experimental structural features discussed above.

There are no vibrational frequencies between 1500 and 2000 cm^{-1} for C_9H_4, $C_{10}H_4$, and $C_{11}H_4$. For $C_{18}H_6$, our results suggest that there should be a strong IR absorption around 1620 cm^{-1}, which is also Raman active, and a Raman band at 1874 cm^{-1}. These frequencies are assigned to the A_1' symmetry C=C stretch plus C—C stretch for the central radialene (1874 cm^{-1}) and the E' symmetry C=C stretch. Comparing our theoretical results for $C_{18}H_6$ with the unsubstituted [3]radialene, for which vibrational spectra are available, the agreement with experiment is very good for both frequencies and symmetry assignments. Experimentally,[8] for the unsubstituted [3]radialene, there is a weak IR absorption around 1634 cm^{-1} and two Raman-active modes at 1800 (very strong, A_1') and 1620 cm^{-1} (very strong, E'); all these have been assigned as C=C stretches by experimentalists.

(ii) Tetraethynylmethane and Its Derivatives. For the tetraethynylmethane, the key question is whether the C≡C bonds are able to contract as much as the 0.04 Å found in the experimental crystal structure.[6] We have studied six tetraethynylmethane derivatives at the DZP SCF level (Figure 3) in order to understand the effect of "crowding" four alkynyl units around a single carbon atom. However, none of the structures showed a contraction comparable to that reported experimentally.[6]

We have studied three conformations of the tris(trimethylsilyl)-substituted tetraethynylmethane: one is the C_3 conformation in Figure 2, while the other two are of C_{3v} symmetry with three methyl groups pointing "up" and "down", respectively. Those three conformations have almost identical bond lengths and are virtually degenerate. The C_3 conformation is 0.06 kcal mol^{-1} lower in energy by the AM1 method; however, the C_3 structure is 0.01 kcal mol^{-1} higher in energy at the DZP SCF level than the C_{3v} conformation with three methyl groups pointing up. For the tris(trimethylsilyl)-substituted tetraethynylmethane, the C≡C bond distances are 1.195 (C≡CSi) and 1.188 Å (C≡CH) at the DZP SCF level. However, it was reported[6] that the C≡C bond distances are 1.14 and 1.16 Å from X-ray diffraction and that steric crowding is responsible for this extraordinary bond contraction.[6] Unfortunately, our theoretical results do not support this explanation. There is only a very slight C≡C bond contraction, at the DZP SCF level of theory, in the tetraethynylmethane derivatives. As indicated in Figure 4a, b, and c, the C≡C bonds contract and the C(sp^3)—C(sp) bond distances increase with the number of alkynyl substitutents. The C≡C bonds in all six tetraethynylmethane derivatives studied (Figure 3) contract exactly 0.004 Å at the DZP SCF level, compared with propyne derivatives (Figure 4) at the same theoretical level. However, the magnitude of the contraction is only one-tenth of the value reported for the crystal structure.[6]

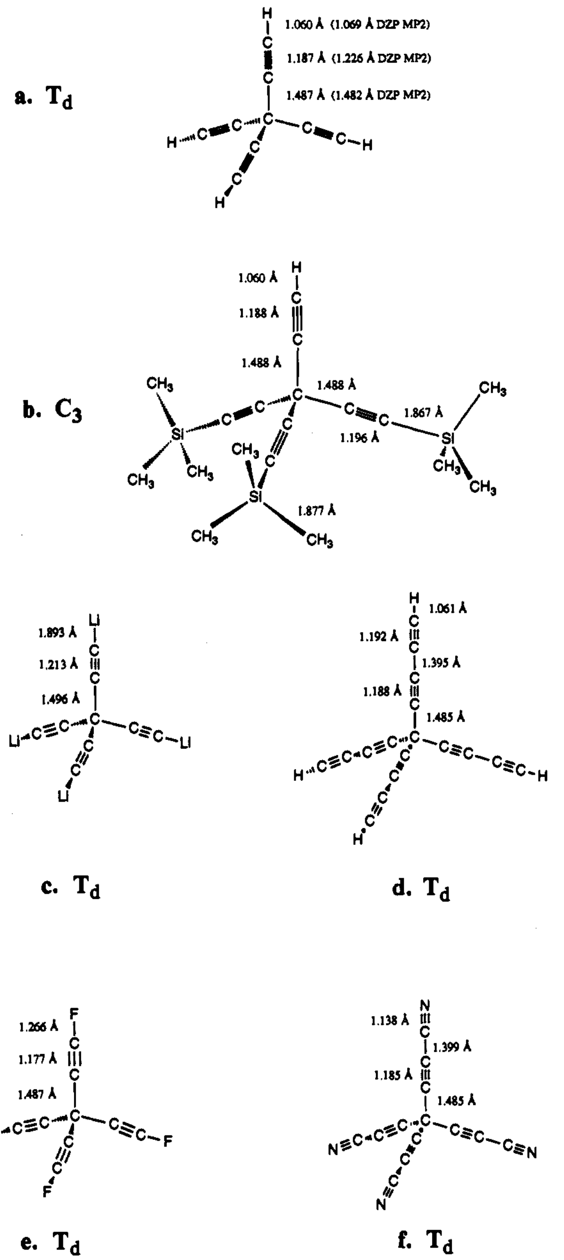

Figure 3. Equilibrium geometries for tetraethynylmethane derivatives at the DZP SCF level of theory for (a) tetraethynylmethane (C_9H_4); (b) the recently synthesized tris(trimethylsilyl)tetraethynylmethane $C_9H[Si(CH_3)_3]_3$; (c) perlithiated tetraethynylmethanate (C_9Li_4); (d) tetrabutadiynylmethane ($C_{17}H_4$); (e) perfluorotetraethynylmethane (C_9F_4); and (f) tetra(cyanoethynyl)methane [$C_9(CN)_4$].

Here a careful evaluation of the reliability of our theoretical results at the DZP SCF level is desired for comparison with the experimental bond distances. Firstly, our theoretical C(sp^3)—C(sp) single bond distances at the DZP SCF level should be longer than the experimental value. For example, in the case of propyne, the C(sp^3)—C(sp) distance (1.474 Å, DZP SCF, Figure 4a)) is longer than the experimental value (1.459 Å).[15] For diethynylmethane, our theoretical C(sp^3)—C(sp) single bond distance is

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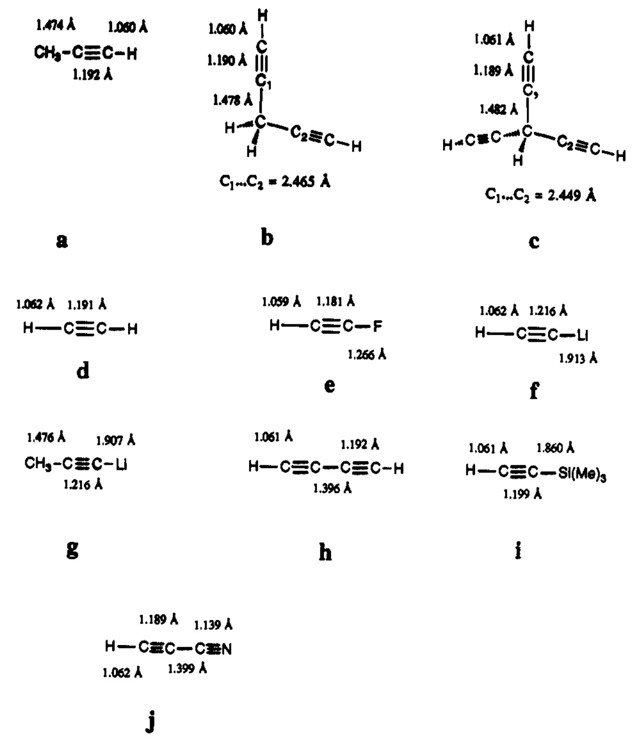

Figure 4. Equilibrium geometries for several alkynes at the DZP SCF level of theory.

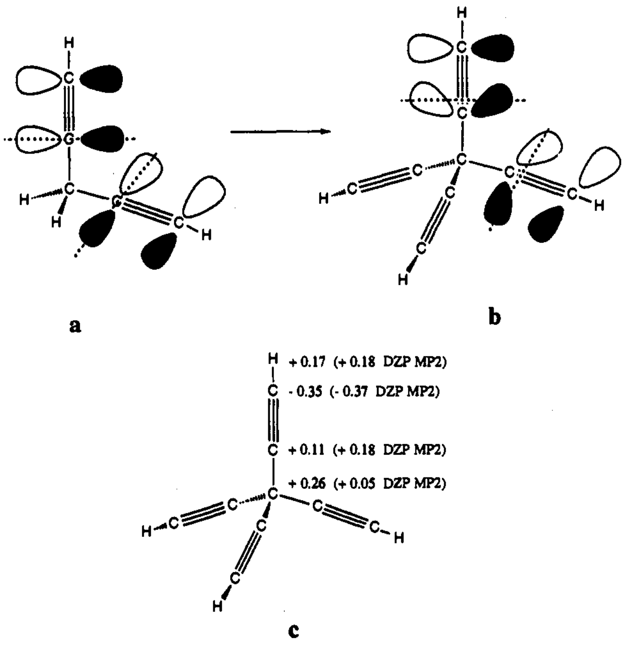

Figure 5. Schematic illustration of the π electron compression in the tetraethynylmethane derivatives. (a) The uncompressed π electron distribution, where the center of electron density is coincident with the nuclei. (b) The compressed π electron distribution, where the center of electron density is not coincident with the nuclei. (c) The Mulliken charge distribution of the tetraethynylmethane molecule at the DZP SCF level of theory.

1.478 Å (DZP SCF, Figure 4b), whereas a comparable X-ray bond distance[4] for the propargylic $C(sp^3)$—$C(sp)$ single bond in tetrapropargylmethane is 1.462 Å. Secondly, our theoretical $C\equiv C$ bond distance should be shorter than the experimental value; this may be illustrated by comparing our theoretical $C\equiv C$ bond distances at the DZP SCF level with those of existing X-ray structures (for example, tetraethynylbutatriene[7] and tetraethynylethylene[1b]). In conclusion, compared to our theoretical geometries, the experimental[6] $C\equiv C$ bond distances are shorter and the $C(sp^3)$—$C(sp)$ single bond distances are slightly longer.

In order to investigate the theory/experiment difference, we also optimized the geometry of tetraethynylmethane at a correlated level of theory (DZP MP2, Figure 3a). However, the difference between the experiment and our theoretical results becomes wider. The $C\equiv C$ bond distance is 1.226 Å at the DZP MP2 level, 0.08 Å longer than the reported experimental value (1.14 Å).[6] Although the MP2 method with much larger basis sets will surely decrease this triple bond distance, the MP2 basis set limit should be longer than 1.20 Å. The $C(sp^3)$—$C(sp)$ single bond distance is 1.482 Å at the DZP MP2 level. These results suggest that the steric crowding of the alkynyl group is even smaller at the DZP MP2 level than at DZP SCF level, consistent with our evaluation of the strain energy for the tetraethynylmethane molecule (see next section).

Crystal packing effects may be one of the reasons for the theory/experiment difference. For example, the $C\equiv C$ bond distances in the X-ray structure of tetraethynylethylene[1b] are distorted to 1.207 and 1.163 Å. However, the experimental $C\equiv C$ bond contraction (1.14 and 1.16 Å) for the tetraethynylmethane is abnormal. Assuming that the experimental results are correct (a dubious assumption), one explanation for the discrepancy between our theoretical structure and the X-ray structure could be the difference between the two methods. Our theoretical structures yield equilibrium internuclear distances, while the X-ray structure is really the distances between the centroids of electron clouds of atoms involved in bond formation.[16] The difference between CC bond lengths measured by neutron diffraction and those measured by X-ray diffraction may be as large as 0.02–0.03 Å.[16] This consideration should be reinforced in the case of the tetraethynylmethane molecule, where the interaction between geminal alkynyl groups may be strong because the nonbonding C···C distances in the tetraethynylmethane derivatives are very short (2.242 Å in C_9H_4). The close contact of geminal alkynyl groups could give rise to π electron compression as illustrated in Figure 5. By this scheme, there is a possibility that the electrons, rather than the nuclei,[6] are pushed outward along the $C\equiv C$ bond, i.e., the electron distribution in the $C\equiv C$ bonds is compressed, which makes the $C\equiv C$ bonds look "contracted" and the $C(sp^3)$—$C(sp)$ distance appear longer in the X-ray diffraction experiment.[6]

The electron compression effect, first noted in our study of the polarizabilities (part C) and energetics (part B) of these acetylenic precursors, has evidence in the aspects of charge distribution and substituent effect as well.

(1) The π electron compression will shift the π electron density toward the outer carbon atoms, leading to the Mulliken charge distribution of Figure 5.

(2) In order to test whether this π electron compression may be operative in the tetraethynylmethane derivatives, we studied four tetraethynylmethane derivatives substituted by Li, F, CN, and $C\equiv CH$ groups, respectively (Figure 3c, d, e, and f). With charge transferred from the lithium atoms to the tetraethynylmethane, the electron compression will increase and the C—C bond distances should increase; while the F, CN, and $C\equiv CH$ substituents should decrease the C—C bond distances due to their electron-withdrawing or conjugation effects. The lithiated tetraethynylmethane showed the expected increase of the C—C bond distance, and the CN and $C\equiv CH$ substitutions showed the expected C—C bond shortening. In the case of perfluorotetraethynylmethane, the C—C bond does not contract as expected. The reason may be that the fluorine, while being a strong σ electron acceptor, is also a π electron donor.[15] The bond distance variance discussed above may involve both the π electron compression effect and simple substituent effects. For example, the C—C bond distance in $CH_3C\equiv CLi$ (Figure 4g) is 0.002 Å longer than that in $CH_3C\equiv CH$ (Figure 4a), a simple substituent effect.

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Table 1. Thermochemical Energies (kcal mol^{-1}) at the DZP MP2 Level of Theory[a]

reaction no.	isodesmic reactions	ΔE_e	ΔE_0	ΔH°
1	$CH_2(C\equiv CH)_2 + 3CH_4 \rightarrow 2HC\equiv CH + 2C_2H_6$	15.2 (13.4)	17.5 (15.7)	16.6 (14.8) 17.2[b]
2	$CH(C\equiv CH)_3 + 5CH_4 \rightarrow 3HC\equiv CH + 3C_2H_6$	21.1 (14.0)	25.5 (18.4)	23.7 (16.6)
3	$CH_2(CH{=}CH_2)_2 + 3CH_4 \rightarrow 2H_2C{=}CH_2 + 2C_2H_6$			12.9[b]
4	$CH(CH{=}CH_2)_3 + 5CH_4 \rightarrow 3CH{=}CH_2 + 3C_2H_6$			-9.8[b]
5	$4CH_3C\equiv CH \rightarrow C(C\equiv CH)_4 + 3CH_4$	7.4 (22.4)	3.4 (18.4)	4.8 (19.8)
6	$4CH_3C\equiv CH + 4HC\equiv C{-}C\equiv CH \rightarrow C(C\equiv C{-}C\equiv CH)_4 + 3CH_4 + 4HC\equiv CH$	3.7 (24.3)	-2.3 (18.5)	0.6 (21.1)
7	$2H_2C(C\equiv CH)_2 \rightarrow C(C\equiv CH)_4 + CH_4$	3.7 (15.1)	1.2 (12.6)	2.1 (13.5)
8	$2CH_3C\equiv CH \rightarrow H_2C(C\equiv CH)_2 + CH_4$	1.9 (3.6)	1.2 (2.7)	1.5 (3.0)
9	$CH_2(C\equiv CH)_2 + CH_3C\equiv CH \rightarrow HC(C\equiv CH)_3 + CH_4$	2.7 (7.5)	1.3 (6.1)	1.8 (6.6)
10	$HC(C\equiv CH)_3 + CH_3C\equiv CH \rightarrow C(C\equiv CH)_4 + CH_4$	2.8 (11.1)	1.0 (9.3)	1.6 (9.6)
11	$C(C\equiv CH)_4 + 4HC\equiv C{-}C\equiv CH \rightarrow C(C\equiv C{-}C\equiv CH)_4 + 4HC\equiv CH$	-3.7 (1.9)	-5.5 (0.1)	-4.1 (1.5)
12	$C(C\equiv CH)_4 + 4HC\equiv C{-}Li \rightarrow C(C\equiv C{-}Li)_4 + 4HC\equiv CH$	8.9 (12.6)	8.6 (12.3)	8.1 (11.8)
13	$C(C\equiv CH)_4 + 4HC\equiv C{-}F \rightarrow C(C\equiv C{-}F)_4 + 4HC\equiv CH$	6.3 (3.9)	5.4 (3.0)	5.1 (2.7)
14	$C(C\equiv CH)_4 + 4HC\equiv C{-}CN \rightarrow C(C\equiv C{-}CN)_4 + 4HC\equiv CH$	2.7 (8.8)	1.0 (7.2)	1.2 (7.3)
15	$C(C\equiv CH)_4 + 3HC\equiv C{-}Si(Me)_3 \rightarrow HC\equiv C{-}C[C\equiv C{-}Si(Me)_3]_3 + 3HC\equiv CH$	(0.9)		
20	$C(C\equiv CH)_4 + 3Si(Me)_4 \rightarrow HC\equiv C{-}C(C\equiv C{-}Si(Me)_3)_3 + 3CH_4$	(-45.3)		
21	$HC\equiv CH + Si(Me)_4 \rightarrow HC\equiv C{-}Si(Me)_3 + CH_4$	-15.6 (-15.4)	-15.2 (-15.0)	-15.0 (-14.8)

[a] The data in parentheses are at the DZP SCF level of theory. [b] The experimental data are based on the heats of formation reported in ref 18.

However, the C—C bond distance in C_9Li_4 (Figure 3c) is 0.009 Å longer than that in C_9H_4 (Figure 3a), indicating the operation of the π electron compression effect.

It is important to realize that even though the π electron compression effect could lead to the difference between the internuclear distance and the distance of the center of the electron density for the tetraethynylmethane derivatives, it is difficult to evaluate such differences quantitatively—for example, through analyzing computed electron densities. Our opinion is that there is still much uncertainty concerning the reliability of the experimental C≡C distances in the tetraethynylmethane derivatives. Therefore, it is necessary to reexamine the X-ray diffraction results. If the C≡C bond contraction is reconfirmed by the X-ray diffraction, then we suggest that neutron diffraction experiments are in order to test the possible π electron compression effects.

B. Thermochemistry of the Precursors. (i) Evaluation of Strain Energy of the Tetraethynylmethane Derivatives. We have mentioned the "crowdedness" caused by attaching four alkynyl to a single carbon atom. Does this crowdedness give rise to strain in the molecules? Since the alkynyl group is one-dimensional, its steric hindrance should be relatively small, for example, far less than that by a $-CH{=}CH_2$ group, as indicated by the energetics of reactions 1–4 (for summary of thermochemical energies at the DZP MP2 level, see Table 1):

$$CH_2(C\equiv CH)_2 + 3CH_4 \rightarrow 2HC\equiv CH + 2CH_3{-}CH_3 \quad (1)$$
$$\Delta H^\circ(\text{expt}) = 17.2 \text{ kcal mol}^{-1}$$

$$CH(C\equiv CH)_3 + 5CH_4 \rightarrow 3HC\equiv CH + 3CH_3{-}CH_3 \quad (2)$$
$$\Delta H^\circ(\text{DZP MP2}) = 23.7 \text{ kcal mol}^{-1}$$

$$CH_2(CH{=}CH_2)_2 + 3CH_4 \rightarrow 2H_2{=}CH_2 + 2CH_3{-}CH_3$$
$$\Delta H^\circ(\text{expt}) = 12.9 \text{ kcal mol}^{-1} \quad (3)$$

$$CH(CH{=}CH_2)_3 + 5CH_4 \rightarrow 3CH{=}CH_2 + 3CH_3{-}CH_3$$
$$\Delta H^\circ(\text{expt}) = -9.8 \text{ kcal mol}^{-1} \quad (4)$$

It is the nature of the C≡C bond that makes it possible for the nonbonding carbons to closely approach each other in the tetraethynylmethane molecule, giving rise to the possible π electron compression.

Strain energies are usually evaluated on the basis of the ΔH° for homodesmotic reactions with strain-free reference molecules. For example, reaction 5 can be used for this purpose. The

$$4CH_3C\equiv CH \rightarrow C(C\equiv CH)_4 + 3CH_4 \quad (5)$$
$$\Delta H^\circ(\text{DZP SCF}) = 19.8 \text{ kcal mol}^{-1};$$
$$\Delta H^\circ(\text{DZP MP2}) = 5 \text{ kcal mol}^{-1}$$

endothermicity of reaction 5 is equal to the strain energy in the tetraethynylmethane. The ΔH° for reaction 5 is 22 kcal mol^{-1} at the DZP SCF level and only 5 kcal mol^{-1} at the DZP MP2 level. Apparently, the SCF method overestimates the strain energy for the C_9H_4 molecule. But the MP2 strain energy deserves further investigation as well, since the strain energy in tetrabutadiynylmethane is even closer to zero at the DZP MP2 level, indicated by the endothermicity of reaction 6:

$$4CH_3C\equiv CH + 4HC\equiv C{-}C\equiv CH \rightarrow C(C\equiv C{-}C\equiv CH)_4 + 3CH_4 + 4HC\equiv CH \quad (6)$$
$$\Delta H^\circ(\text{DZP SCF}) = 24.3 \text{ kcal mol}^{-1};$$
$$\Delta H^\circ(\text{DZP MP2}) = 0.6 \text{ kcal mol}^{-1}$$

The question here is whether the strain energies for the C_9H_4 and the $C_{17}H_4$ molecules are really so small.

Firstly, the reliability of the DZP MP2 method has to be confirmed by comparison with experimental ΔH°. As can seen from reactions 1, the theoretical result at the DZP MP2 level is within 1 kcal mol^{-1} of experiment.

$$H_2C(C{\equiv}CH)_2 + 3CH_4 \rightarrow 2CH_3{-}CH_3 + 2HC{\equiv}CH \qquad (1)$$

$$\Delta H^\circ(\text{expt}) = 17.2\ \text{kcal mol}^{-1};$$

$$\Delta H^\circ(\text{DZP MP2}) = 16.6\ \text{kcal mol}^{-1}$$

Secondly, we employed reaction 7 to show that our "strain-free reference molecule" had been chosen properly. Using $CH_2(C{\equiv}CH)_2$ as a strain-free molecule gives an even smaller strain energy. Actually, there is only a small increase in the strain energy as the alkynyl substitution in methane increases. This can be illustrated by reactions 8–10.

$$2H_2C(C{\equiv}CH)_2 \rightarrow C(C{\equiv}CH)_4 + CH_4 \qquad (7)$$

$$\Delta H^\circ(\text{DZP MP2}) = 2.1\ \text{kcal mol}^{-1}$$

$$2CH_3C{\equiv}CH \rightarrow H_2C(C{\equiv}CH)_2 + CH_4 \qquad (8)$$

$$\Delta H^\circ\ (\text{DZP MP2}) = 1.5\ \text{kcal mol}^{-1}$$

$$CH_2(C{\equiv}CH)_2 + CH_3C{\equiv}CH \rightarrow HC(C{\equiv}CH)_3 + CH_4$$

$$\Delta H^\circ(\text{DZP MP2}) = 1.8\ \text{kcal mol}^{-1} \qquad (9)$$

$$HC(C{\equiv}CH)_3 + CH_3C{\equiv}CH \rightarrow C(C{\equiv}CH)_4 + CH_4 \qquad (10)$$

$$\Delta H^\circ(\text{DZP MP2}) = 1.6\ \text{kcal mol}^{-1}$$

Thus, the thermochemical data confirm that the tetraethynylmethane molecule is not highly strained. The small amount of strain is probably caused by the π electron compression, which may be "soft".

(ii) Substituent Effects on the Strain in the Tetraethynylmethane Derivatives. The substituent effects on the strain in the tetraethynylmethane derivatives show more support for the hypothesis of the π electron compression effects:

$$C(C{\equiv}CH)_4 + 4HC{\equiv}C{-}C{\equiv}CH \rightarrow C(C{\equiv}C{-}C{\equiv}CH)_4 + 4HC{\equiv}CH \qquad (11)$$

$$\Delta H^\circ(\text{DZP SCF}) = 1\ \text{kcal mol}^{-1};$$

$$\Delta H^\circ(\text{DZP MP2}) = -4\ \text{kcal mol}^{-1}$$

$$C(C{\equiv}CH)_4 + 4HC{\equiv}C\text{-}Li \rightarrow C(C{\equiv}C{-}Li)_4 + 4HC{\equiv}CH \qquad (12)$$

$$\Delta H^\circ(\text{DZP SCF}) = 11.9\ \text{kcal mol}^{-1};$$

$$\Delta H^\circ(\text{DZP MP2}) = 8.1\ \text{kcal mol}^{-1}$$

The exothermicity of reaction 11 indicates that the π electron compression is relieved due to the greater π electron flexibility in the tetrabutadiynylmethane ($C_{17}H_4$) molecule, while the endothermicity of reaction 12 indicates that the π electron compression is increased due to the higher electron density caused by the electron transfer from lithium.

The effects of the two electron-withdrawing groups in our study, -F and -CN, are more complex. There are two factors that contribute to the energy change for reactions 13 and 14:

$$C(C{\equiv}CH)_4 + 4HC{\equiv}C{-}F \rightarrow C(C{\equiv}C{-}F)_4 + 4HC{\equiv}CH \qquad (13)$$

$$\Delta H^\circ(\text{DZP SCF}) = 3.9\ \text{kcal mol}^{-1};$$

$$\Delta H^\circ(\text{DZP MP2}) = 6.3\ \text{kcal mol}^{-1}$$

$$C(C{\equiv}CH)_4 + 4HC{\equiv}C{-}CN \rightarrow C(C{\equiv}C{-}CN)_4 + 4HC{\equiv}CH \qquad (14)$$

$$\Delta H^\circ(\text{DZP SCF}) = 8\ \text{kcal mol}^{-1};$$

$$\Delta H^\circ(\text{DZP MP2}) = 1.2\ \text{kcal mol}^{-1}$$

The difference between the endothermicities of reactions 13 and 14 is another indication of the importance of the π electron compression. Since the central carbon atom has a relatively large positive charge (+0.26, see Figure 5), a σ electron-withdrawing effect will destabilize the molecule. However, the π electron-withdrawing effect will stabilize the molecule by relieving the π electron compression. The -CN group, which in general is more electron-withdrawing than the fluorine atom due to inductive and resonance effects, should have made reaction 14 more endothermic than reaction 13. However, due to the π conjugation ability of the CN group, which is expected to decrease the π electron compression, reaction 14 is almost thermoneutral.

Finally, as is shown by the energetics of reaction 15, the introduction of three silyl groups does not give rise to additional steric hindrance in the tetraethynylmethane molecule.

$$C(C{\equiv}CH)_4 + 3HC{\equiv}C{-}Si(Me)_3 \rightarrow HC{\equiv}C{-}C[C{\equiv}C{-}Si(Me)_3]_3 + 3HC{\equiv}CH \qquad (15)$$

$$\Delta E_e(\text{DZP SCF}) = 0.9\ \text{kcal mol}^{-1}$$

(iii) Evaluation of the Conjugation Energy of Cross-Conjugated Molecules. The molecular conjugation energy may be evaluated on the basis of the bond separation energies via isodesmic reactions.[15] However, in recent years such discussions, have been made in terms of group additivity[17] rather than bond additivity. Therefore, we chose vinylacetylene ($H_2C{=}CHC{\equiv}CH$) as a reference molecule to study the conjugation energy for these cross-conjugated molecules. The homodesmotic reactions[17] we employed are the following:

$$4H_2C{=}CHC{\equiv}CH \rightarrow C_{10}H_4 + 3H_2C{=}CH_2 \qquad (16)$$

$$\Delta H^\circ(\text{DZP SCF}) = 8.6\ \text{kcal mol}^{-1};$$

$$\Delta H^\circ(\text{DZP MP2}) = -1.7\ \text{kcal mol}^{-1}$$

$$H_2C{=}C{=}CH_2 + 4H_2C{=}CHC{\equiv}CH \rightarrow C_{11}H_4 + 4H_2C{=}CH_2 \qquad (17)$$

$$\Delta H^\circ(\text{DZP SCF}) = 17.2\ \text{kcal mol}^{-1};$$

$$\Delta H^\circ(\text{DZP MP2}) = 9.0\ \text{kcal mol}^{-1}$$

$$H_2C{=}C{=}C{=}CH_2 + 4H_2C{=}CHC{\equiv}CH \rightarrow C_{12}H_4 + 4H_2C{=}CH_2 \qquad (18)$$

$$\Delta H^\circ(\text{DZP SCF}) = 12.2\ \text{kcal mol}^{-1};$$

$$\Delta H^\circ(\text{DZP MP2}) = 0.2\ \text{kcal mol}^{-1}$$

$$C_6H_6\ ([3]\text{radialene}) + 6H_2C{=}CHC{\equiv}CH \rightarrow C_{18}H_6 + 6H_2C{=}CH_2 \qquad (19)$$

$$\Delta H^\circ(\text{DZP SCF}) = 10.5\ \text{kcal mol}^{-1};$$

$$\Delta H^\circ(\text{DZP MP2}) = -12.3\ \text{kcal mol}^{-1}$$

It may be seen from the above reactions (also in Table 2) that the conjugation interaction for two planar molecules ($C_{10}H_4$ and $C_{12}H_4$) does not change with respect to that for $H_2C{=}CHC{\equiv}CH$, indicated by the very small enthalpy changes for reactions 16 and 18. However, reaction 17 is 9.0 kcal mol^{-1} endothermic, indicating that the extent of conjugation is decreased due to its nonplanar geometry. On the other hand, reaction 19 is 12.3 kcal mol^{-1} exothermic; therefore, the conjugation energy for the $C_{18}H_6$ molecule is increased with respect to that for $H_2C{=}CHC{\equiv}CH$, probably because the strain in the central radialene has been released partially.

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Table 2. Thermochemical Energies at the DZP MP2 Level of Theory[a]

compound	homodesmotic reaction no.	$\Delta H_f°$ [b]		strain energy			conjugation energy[c]		
		AM1	DZP MP2	ΔE_e	ΔE_0	$\Delta H°$	ΔE_e	ΔE_0	$\Delta H°$
tetraethynylmethane (C_9H_4)	5	228.8	236.6	7.4 (22.4)	3.3 (18.4)	4.8 (19.8)			
tetraethynylethylene ($C_{10}H_4$)	16	233.9	246.8				−0.9	−2.7	−1.7
tetraethynylallene ($C_{11}H_4$)	17	268.9	288.6				9.2	7.8	9.0
tetraethynylbutatriene ($C_{12}H_4$)	18	295.8	317.2				0.4	−1.0	0.2
tetrabutadiynylmethane ($C_{17}H_4$)	6	436.1	428.3	3.7 (24.3)	−2.3 (18.5)	0.6 (21.1)			
hexaethynyl[3]radialene ($C_{18}H_4$)	19	433.6	437.7				−11.2	−14.7	−12.3

[a] All values are in kcal mol^{-1}; the MP2 energies are based on the DZP SCF geometries. The values in parentheses were obtained at the DZP SCF level of theory. [b] The required experimental $\Delta H_f°$ values for the evaluation are taken from ref 18; the $\Delta H_f°$ (kcal mol^{-1}) are as follow: CH_4, −17.8 kcal mol^{-1}; ethylene, 14.5 kcal mol^{-1}; acetylene, 54.5 kcal mol^{-1}; propyne, 44.6 kcal mol^{-1}; allene, 45.6 kcal mol^{-1}; butatriene, 83 kcal mol^{-1}; [3]radialene, 99 kcal mol^{-1}. [c] With respect to $H_2C{=}CHC{\equiv}CH$.

(iv) Evaluation of the Heats of Formation ($\Delta H_f°$) for the Acetylenic Precursor Molecules. For these highly unsaturated molecules, the heat of formation is an important property which reflects their thermochemical stability or lack of stability. Based on the evaluation of the strain energy and conjugation energies, the $\Delta H_f°$ values for those molecules are readily evaluated as follows:

$$\Delta H_f°(\text{target multiacetylene molecules}) = \sum \Delta H_f°(\text{reactants}) - n\Delta H_f°(\text{byproducts}) + \Delta H°(\text{enthalpy changes for the homodesmotic reactions})$$

The heats of formation of the reactants and of methane are taken from ref 18. As expected, all these molecules have a very high $\Delta H_f°$ (Table 2), thus indicating that those molecules are thermodynamically unstable, and *great care should be taken in handing such compounds.*

How can the protecting effect of the silyl group on these highly reactive molecules be understood? The common explanation is the bulkiness of the silyl group. However, we have an additional explanation in terms of the thermochemistry. Via reaction 20, we are able to evalaute the $\Delta H_f°$ for the recently synthesized $HC{\equiv}C{-}C[C{\equiv}C{-}Si(Me)_3]_3$ molecule to be 77 kcal mol^{-1} at the DZP SCF level. The corresponding value evaluated by the semiempirical AM1 method is 50 kcal mol^{-1}. The relatively small $\Delta H_f°$ is the thermodynamic explanation for the protecting effect of the silyl group. There are two mechanisms for the $\Delta H_f°$-lowering effect of the silyl group. The first one is the negative $\Delta H_f°$ of the $Si(Me)_4$ (−55.7 kcal mol^{-1}),[18] which contributes two-thirds of the $\Delta H_f°$ decrease in the heats of formation for the substituted molecule. The second mechanism is the hyperconjugation stabilizing effect of the silyl group on the alkynyl group, which contributes one-third of the $\Delta H_f°$ decrease. The hyperconjugation effect may be shown by reactions 20 and 21:

$$C(C{\equiv}CH)_4 + 3Si(Me)_4 \rightarrow HC{\equiv}C{-}C[C{\equiv}C{-}Si(Me)_3]_3 + 3CH_4 \quad (20)$$

$$\Delta E_e(\text{DZP SCF}) = -45.3 \text{ kcal mol}^{-1}$$

$$HC{\equiv}CH + Si(Me)_4 \rightarrow HC{\equiv}C{-}Si(Me)_3 + CH_4 \quad (21)$$

$$\Delta H°(\text{DZP SCF}) = -14.8 \text{ kcal mol}^{-1}; \quad \Delta H°(\text{DZP MP2}) = -15 \text{ kcal mol}^{-1}$$

The conjugation energy between the alkynyl group and the trimethylsilyl group is −15.0 kcal mol^{-1} at the DZP MP2 level. This agrees with the finding[19] that SiH_3 is able to stabilize some radicals and carbenium ions by 10–20 kcal mol^{-1} at the DZP MP2 level.

Table 3. Diffuse Gaussians Functions Added to the DZ and STO-3G Basis Sets

label	diffuse functions for C and H[a]	exponents				
		carbon			hydrogen	
		ζ_s	ζ_p	ζ_d	ζ_s	ζ_p
A	DZ + p, d; s, p		0.24	0.04	0.018	0.018
B	DZ + p, d; s, p		0.05	0.05	0.05	0.05
C	STO-3G + s, p, d; s, p	0.05	0.05	0.05	0.05	0.05
D	STO-3G + p, d; s, p		0.38	0.026	0.04	0.027
E	STO-3G + p, d; s, p		0.05	0.05	0.05	0.05
F	STO-3G + p, d; s		0.05	0.05	0.05	
G	STO-3G + p, d; s		0.05	0.05	0.04	

[a] Carbon and hydrogen functions separated by a semicolon for each entry.

C. (Hyper)Polarizabilities of the Acetylenic Precursor Molecules. (i) Basis Set Evaluation. Basis set quality is very important in predicting the electrical properties of molecules. It is well known that a very large atomic orbital (AO) basis set plus diffuse functions is needed to obtain accurate electrical properties for small molecules. This makes the computational evaluation of α and γ very difficult. Recently, several publications have shown that the small basis set plus proper diffuse functions can describe molecular polarizabilities quite accurately, providing that molecular geometries are optimized accurately.[13,20,21] Hurst, Dupuis, and Clementi[13] showed that a small augmented version of the 6-31G basis set (6-31G+PD basis with p- and d-type diffuse functions, on carbon) can provide a good description of α and γ. Spackman[20] also obtained accurate static dipole polarizabilities with 6-31G(+sd+sp) basis sets. Dupuis[21] et al. extended the method further to use even smaller basis sets, namely, the 3-21G basis with diffuse s, p, and d functions for the evaluation of both α and γ. Their results yield quite accurate values for the polarizability (α). However, the evaluation of γ by *ab initio* methods remain a problem. Often, the $\bar{\gamma}$ values evaluated by *ab initio* methods are only around 50% of the experimental value.[20,21]

In the present research, we have examined the behavior of STO-3G basis sets augmented with diffuse functions. Table 3 lists the Gaussian functions used to enlarge the DZ and also the STO-3G basis. The theoretical results for acetylene are listed in Table 4. At first, based on the STO-3G basis set, we added s-, p-, and d-type diffuse functions to the carbon atoms and s- and p-type functions to hydrogen atoms (basis set C). The results

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Table 4. Results for C_2H_2 with DZ and STO-3G Basis Sets Augmented by Diffuse Functions[a]

	basis set										
	STO-3G	DZ	DZP	A	B	C	D	E	F	G	exp[21]
energy (hartrees)	75.8184	76.7989	76.8315	76.8102	76.8011	75.8824	75.8683	75.8824	75.8822	**75.8821**	
$\bar{\alpha}$	7.3	14.7	15.7	18.9	20.2	22.2	20.5	22.2	22.1	**22.1**	22.7
$\alpha_{xx} = \alpha_{yy}$	2.0	7.4	8.9	13.2	15.1	19.3	18.1	19.3	19.1	**19.1**	18.8
α_{zz}	18.0	29.2	29.4	30.4	30.5	28.0	25.3	28.0	28.0	**27.9**	30.6
$\bar{\gamma}$	20.1	128	73.5	7813	5445	7274	20378	7273	7119	**7243**	20 450
$\gamma_{xxxx} = \gamma_{zzzz}$	−4	111	78.4	10 494	6379	7277	25 483	7277	7255	**7293**	
γ_{yyyy}	−122	−506	−499	2004	2763	3922	4227	3921	3356	**3045**	
$\gamma_{xxyy} = \gamma_{yyzz}$	58	213	164.2	2270	1862	3260	7440	3259	3222	**3341**	
γ_{xxzz}	−1.0	37	26	3498	2116	2425	8487	2425	2418	**2430**	

[a] Basis sets labels as in Table 3. Atomic units (au) are used. For α, 1 au $\equiv e^2a_0^2E_h^{-1} \approx 1.6488 \times 10^{-41}$ C^2 m^2 J^{-1}; for γ, 1 au $\equiv e^4a_0^4E_h^{-3} \approx 6.2360 \times 10^{-65}$ C^2 m^2 J$^{-1} \approx 5.0366 \times 10^{-40}$ esu. Orientationally averaged values are $\bar{\alpha} = {}^1/_3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$ and $\bar{\gamma} = {}^1/_5(\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{xxzz} + 2\gamma_{yyzz})$.

Table 5. Theoretical Results of Molecular Polarizabilities and Hyperpolarizabilities Evaluated Using the STO-3G Basis Set with Diffuse Functions (G)

						exptl results		other works	
molecule	$\bar{\alpha}$	α_{xx}	α_{yy}	α_{zz}	$\bar{\gamma}$	$\bar{\alpha}$	$\bar{\gamma}$	$\bar{\alpha}$	$\bar{\gamma}$
CH_4	11.6	11.6	11.6	11.6	3022	17.3[e]		16.0,[b] 16.3[e]	1743[b]
$CH_3{-}CH_3$	21.4	20.9	20.9	22.3	5241	29.8[c]	3772[c]	24.0,[c] 26.9[e]	3531[c]
$H_2C{=}CH_2$	26.5	32.6	21.9	25.0	9047	27.8[e]	9000[a]	28.1,[e] 28.1[b]	
allene (C_3H_4)	40.1	29.9	29.9	60.5	13 100	40.4[c]		37.9,[c] 40.5[e]	8253[c]
diacetylene (C_4H_2)	44.4	30.2	30.2	72.9	15 800			49.0[d]	9744[d]
butadiene (C_4H_6)	53.1	37.4	80.5	41.4	21 350	58.3[a]	27 400[a]	53.3[a]	14 846[a]
benzene	64.1	70.8	70.8	50.8	18 976	69.7[f]	18 608[f]		
propyne ($CH_3C{\equiv}CH$)	31.6	26.6	26.6	41.4	9470				
butatriene (C_4H_4)	61.4	35	110	38.5	21 060				

[a] Reference 13. [b] Reference 23. [c] Reference 21. [d] Reference 24. [e] Reference 20. [f] Reference 25.

Table 6. Analysis of Molecular Polarizabilities, Hyperpolarizabilities, and Molecular Orbital Energies Evaluated Using the STO-3G Basis Set with Diffuse Functions (G)

					nonadditivity		
molecule	$\bar{\alpha}$	$\bar{\gamma}$	ϵ_{HOMO}	ϵ_{LUMO}	isodesmic reaction	$\Delta\bar{\alpha}$	$\Delta\bar{\gamma}$
tetraethynylmethane (C_9H_4)	82.26	21 030	−0.3994	0.0585	*a*	−9.26	−7470
tetraethynylethylene ($C_{10}H_4$)	112.5	46 030	−0.3144	0.0503	*b*	6.08	11 191
tetraethynylallene ($C_{11}H_4$)	125.12	39 980	−0.3490	0.0548	*c*	5.1	1088
tetraethynylbutatriene ($C_{12}H_4$)	172.86	73 210	−0.2939	0.0139	*d*	31.59	26 360

[a] $4CH_3C{\equiv}CH \rightarrow C(C{\equiv}CH)_4 + 3CH_4$. [b] $H_2C{=}CH_2 + 4HC{\equiv}CH + 4CH_3{-}CH_3 \rightarrow C_{10}H_4 + 8CH_4$. [c] $H_2C{=}C{=}CH_2 + 4HC{\equiv}CH + 4CH_3{-}CH_3 \rightarrow C_{11}H_4 + 8CH_4$. [d] $H_2C{=}C{=}C{=}CH_2 + 4HC{\equiv}CH + 4CH_3{-}CH_3 \rightarrow C_{12}H_4 + 8CH_4$.

obtained that way are essentially as good as those reported in other publications with larger basis sets.[20–25] Finally, we found that two sets of diffuse functions (s for carbon and p for hydrogen) can be deleted without serious effects on the final accuracy (basis sets F and G). Therefore, we chose basis set G for the evaluation of the (hyper)polarizabilities for the large molecules in our study.

We have examined basis set G for other small molecules, and the results are reported in Table 5. It is very encouraging that the smallest basis set with only three diffuse functions could give such reasonable results for the polarizability. Our polarizability results are usually comparable with other results obtained using larger basis sets.[20–25] However, the values reported here for $\bar{\gamma}$ are among the best, with highest percentages of the experimental $\bar{\gamma}$ values, reported to date.[20–25] It is worth noting that our $\bar{\gamma}$ values for the ethylene and benzene molecules are almost the same as the experimental values.[13,25]

Even though the basis set G gives superior results for unsaturated hydrocarbons, it is inadequate for saturated hydrocarbons, for example, methane and ethane. However, this is not a debilitating problem, since virtually all molecules where the (hyper)polarizability is of interest are unsaturated.

(ii) Importance of the Electron Flexibility for the (Hyper)-Polarizabilities. The mechanism of the second-order nonlinear response γ has been attributed to the *electron flexibility* in extended π orbital systems.[13] The second nonlinear response γ reflects the effects of π electron conjugation.[22] The more extended the π electron delocalization, the larger the (hyper)polarizability. This trend is true for the increase of (hyper)polarizabilities in the series $C_{10}H_4$, $C_{11}H_4$, and $C_{12}H_4$. It is interesting to note that the $\bar{\gamma}$ value for $C_{11}H_4$ is lower than that of $C_{10}H_4$, another indication that the π electron delocalization for the $C_{11}H_4$ molecule is less effective. This result suggests that a proposed polymeric network with orthogonal chains[1] may not be particularly useful in nonlinear optical applications.

The $\bar{\gamma}$ value, rather than the $\bar{\alpha}$ value, seems qualitatively correlated with the orbital energy of the HOMO and the LUMO. The higher the HOMO energy or the smaller the energy gap (at the SCF level with basis set G), the larger the $\bar{\gamma}$ value (Table 6).

More insight into the structure–property relationships may be achieved by analyzing the nonadditivity of the molecular (hyper)-

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polarizability. Le Fevre has studied the "exaltation" of the polarizability in conjugated systems. Similarly, by comparing the change of the overall (hyper)polarizability in the isodesmic reactions leading to the target molecules, we may be able to obtain information about the effects appearing when the acetylenic groups are connected to other groups. The data are listed in Table 6 as $\Delta\bar{\alpha}$ and $\Delta\bar{\gamma}$, which indicate the net increase of polarizability and hyperpolarizability, respectively, and are calculated as follows:

$$\Delta\bar{\alpha} \text{ (or } \bar{\gamma}) = \sum \bar{\alpha} \text{ (or } \bar{\gamma})\text{(products)} - \sum \bar{\alpha} \text{ (or } \bar{\gamma})\text{(reactants)}$$

This method may give a reliable prediction of the change of (hyper)polarizability. For example, both $\Delta\bar{\alpha}$ and $\Delta\bar{\gamma}$ are found to be close to zero for reaction 22:

$$CH_3C{\equiv}CH + CH_4 \rightarrow CH_3{-}CH_3 + HC{\equiv}CH \quad (22)$$
$$\Delta\bar{\alpha} = 0.32 \text{ au}; \quad \Delta\bar{\gamma} = 0.23 \text{ au}$$

The result is quite reasonable, considering that there is not much change in the π electron system in reaction 22.

As indicated in Table 6, the incorporation of four acetylenic groups into C_2H_4 and C_4H_4 increases the polarizabilities. However, for $C_{11}H_4$, which has a nonplanar configuration and smaller conjugation energy, the $\Delta\bar{\alpha}$ and $\Delta\bar{\gamma}$ values are smaller, consistent with its less-effective conjugation. However, there is no simple relationship between the conjugation energy and the $\Delta\alpha(\gamma)$. The $C_{12}H_4$ molecule, whose conjugation energy is less than that for the $C_{10}H_4$ molecule, has much larger $\Delta\alpha(\gamma)$ values than the $C_{10}H_4$ molecule.

Finally, the discussion about the $\Delta\bar{\alpha}$ and $\Delta\bar{\gamma}$ values for the C_9H_4 molecule is very important. A finding here is that the $\Delta\bar{\alpha}$ and $\Delta\bar{\gamma}$ values for the C_9H_4 molecule are negative, the values being $\Delta\bar{\alpha} = -9.3$ au; $\Delta\bar{\gamma} = -7470$ au. This means that the conjunction of four acetylenic groups at a single carbon atom decreases the (hyper)polarizability of the system. Since the $\bar{\alpha}$ and $\bar{\gamma}$ are related with the flexibility of π electrons, the results suggest that the π electrons' flexibility is decreased in the C_9H_4 molecule. This fact supports our argument that the π electrons are compressed in the tetraethynylmethane derivatives. The π electron compression will cause the π electrons to be more localized within the C≡C bond and decrease the π electron flexibility, therefore decrease the (hyper)polarizabilities. This is a direct evidence that the strain in the C_9H_4 molecule is caused by π electron compression.

4. Conclusions

Several kinds of acetylenic precursors to multidimensional carbon networks have been studied. Special attention has been paid to the π electron delocalization and compression in those molecules.

The geometries and vibrational frequencies of $C_{11}H_4$, $C_{12}H_4$, and $C_{18}H_6$ are obtained at the DZP SCF level. Excellent agreement with the experimental[7] geometry and vibrational frequencies for the tetraethynylbutatriene ($C_{12}H_4$) molecules has been achieved. The conjugation interaction for two planar molecules ($C_{10}H_4$ and $C_{12}H_4$) does not change with respect to that for the $H_2C{=}CHC{\equiv}CH$. However, the extent of conjugation in the $C_{11}H_4$ is decreased due to its nonplanar geometry. The conjugation energy for the $C_{18}H_6$ molecule is increased with respect to that for $H_2C{=}CHC{\equiv}CH$, probably because the strain in central radialene has been released partially. The HOMO energy and nonadditivity of (hyper)polarizability are lower for $C_{11}H_4$ than those for other planar molecules. The heats of formation for the precursors are evaluated, being 236, 246, 289, 317, and 438 kcal mol^{-1} for the C_9H_4, $C_{10}H_4$, $C_{11}H_4$, $C_{12}H_4$, and $C_{18}H_6$ molecules, respectively. The heat of formation for the tris(trimethylsilyl)-substituted tetraethynylmethane decreases to 76 kcal mol^{-1}, partially due to the hyperconjugation effect of the TMS groups. The hyperconjugation between the alkynyl group and the TMS group is estimated to be 15 kcal mol^{-1}.

The derivatives of the tetraethynylmethane have been examined careful, including the structure and the substituent effects. The alkynyl bond contraction in the tris(trimethylsilyl)-substituted tetraethynylmethane, suggested by experiments,[6] has not been reproduced by present research. Our theoretical C≡C bond distances in the molecule, 1.188 Å for C≡CH and 1.193 Å for the C≡C(TMS) bond, are about 0.04 Å longer than those observed by X-ray diffraction.[6] In this sense, we suggest that there is a great uncertainty about the experimental C≡C bond distance in the tris(trimethylsilyl)-substituted tetraethynylmethane molecule.

However, it seems that there is a novel phenomenon, π electron compression, operating in the tetraethynylmethane. The basic idea for the π electron compression is summarized as follows. Since the alkynyl bonds appear in close vicinity in the tetraethynylmethane molecule, the π electrons, which are relatively flexible, are pushed outward along the C≡C bond. One of the consequences of such π electron distortion might be the shorter C≡C bond distance observed by X-ray diffraction,[6] a technique based on the measurement of electron density rather than internuclear distance. Therefore, it is necessary to reexamine the X-ray diffraction results. If the C≡C bond contraction is reconfirmed by X-ray diffraction, then we suggest that a neutron diffraction experiment, which should give proper internuclear distances, is in order to test the possible π electron compression effect.

The hypothesis, π electron compression in the tetraethynylmethane molecule, is supported by its negative nonadditivity of (hyper)polarizabilities and the substituent effects on its structure and energetics. The nonadditivity of (hyper)polarizabilities for the C_9H_4 molecule, $\Delta\bar{\alpha} = -9.3$ au; $\Delta\bar{\gamma} = -7470$ au (Table 6), probably results from the π electron compression effect. The strain energy of the tetraethynylmethane molecule is estimated to be only 4.8 kcal mol^{-1} at the DZP MP2 level. However, the substitution of hydrogen atoms in the C_9H_4 molecules by lithium atoms increases the C—C bond distances and the strain energy by 8 kcal mol^{-1} at the DZP MP2 level; C≡CH groups shorten the C—C distances and decrease the strain energy by 4.2 kcal mol^{-1}; -CN groups shorten the C—C bond distances and increase the strain energy by 1.2 kcal mol^{-1}; while fluorine atoms do not change the C—C distances but increase the strain energy by 6.3 kcal mol^{-1}. Those substituent effects are consistent with the π electron compression effect.

In order to evaluate the (hyper)polarizabilities for the molecules studied here, the STO-3G basis sets augmented with diffuse functions (p and d functions for carbon and s function for hydrogen atoms) were tested, and it was found that such small basis sets may be sufficient to describe the (hyper)polarizabilities for conjugated hydrocarbons.

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