Polyacetylenes and Cumulenes, Potential Elements for Molecular Machines and Precursors of Carbon Clusters: A Theoretical Study

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Dedicated to Professor *Jack D. Dunitz*, a pioneer in science, on the occasion of his 80th birthday

A recently described very simple procedure for estimating *Hartree – Fock* (*H. F.*) energy and accurate nonrelativistic energy has been used with simple hydrocarbons possessing C=C or C≡C bonds and for the acetylene dimer. Experimental characteristics (heats of formation, ionization potentials, electron affinities), structural features, and reactivity have been discussed in terms of quantum-chemistry characteristics at the *H. F.* level and also at a level including a part of electron correlation. Deviations from linearity with derivatives of long polyacetylenes and cumulenes are ascribed to the lowest-energy deformation vibrations, which decrease rapidly when passing from short to long acetylenic and cumulenic chains. The role of derivatives and heteroanalogues of hydrocarbons under study in atmospheric and interstellar chemistry is briefly mentioned. Derivatives with enhanced stability represent potentially promising construction materials for molecular devices and also resources for the preparation of defined clusters of C-atoms.

Introduction. – The purpose of this study is fourfold. First, it is connected with our recent work dealing with a simple extrapolation scheme for estimating *H. F.* and accurate nonrelativistic energies of atoms and molecules [1]. Second, infinite chains of various sorts of organic polymers attracted our attention as conductors and semi-conductors already long time ago [2]. The systems studied in this paper represent, on the one hand, the first members of a series limiting at infinitely conjugated sp C-atom chains, and, on the other hand, especially the analogues thereof, represent rods for the potential connection of building elements of molecular machines [3]. Third, the species under study may serve as starting materials for preparing various sorts of C-atom clusters. Finally, some of the above-named hydrocarbons and derivatives thereof play a significant role in atmospheric and interstellar chemistry [4].

To keep the size of this literature survey reasonable, we quote papers assuming, in our opinion, a key position in the area. These papers and references cited therein offer a rather complete picture of the situation. It is remarkable how much attention the realm of acetylenes, cumulenes, and derivatives thereof has attracted in recent years [5].

It was *Kloster-Jensen* in the *Heilbronner* group who synthesized [6] in the seventies dihalodiacetylenes and halomethylacetylenes, in connection with photoelectron and vibrational spectroscopy, and, moreover, di- through pentaacetylene and recorded their electronic and photoelectron spectra. They also included a warning concerning explosiveness of triacetylene and quoted in this connection a work [7a] in which remarkable violence of detonations of triacetylene is mentioned. (Risk of violent detonation is mentioned in several papers by *Gladysz*, *vide infra*.)

Extensive preparative work and research on acetylenic compounds was carried out in the second half of the forties and in the fifties by *Armitage, Whiting*, and co-workers [7]. Polyynes of the series $H-(C{\equiv}C)_n-H$ ($n = 4$ to 10, and 12) were prepared in a solution by oxidative coupling of silyl-protected terminal alkynes [8]. The longest-wavelength bands in electronic spectra of these acetylenes and of their mono- and bis(triethylsilyl) derivatives were recorded.

Extensive attention was paid recently to several series of disubstituted α,ω-diphenylpolyynes of up to ten conjugated $C{\equiv}C$ bonds. Besides other features, NMR and electronic spectra were studied [9].

Gao and *Goroff* [10a] prepared iodine-capped acetylenes with three and four $C{\equiv}C$ bonds in good yield. These acetylenes explode when heated in a melting-point capillary. Intermediate formation of explosive silver alkynide (undesirable in a larger-scale synthesis) has been overcome [10b] by a new procedure that permits scaling-up.

An impressive set of α,ω-dicyanopolyynes was prepared, and some physical characteristics and computational features were established [11]. These rod-shaped species represent members of a series that should terminate in an infinite chain of sp-hybridized C-atoms.

Extensive sets of polyacetylenes capped with transition metal complexes were prepared and investigated by *Gladysz* and co-workers [12]. Remarkable polyynediyl chains (C_6-C_{20}) that span two Re-containing end groups were described [12a]. In 1999, the structure of a diplatinum complex of hexaacetylene was established by X-ray crystallography [12c]. Two years later, a crystal structure of a Pt complex of C_{16} polyacetylene was revealed [12d]; in both instances, the chains are slightly bent. In [12d], the authors call attention to increasing explosiveness of higher homologues of diacetylene. It turned out that Ir complexes of butatriene are also bent [13]. A slightly twisted structure was revealed by structural analysis for (dodecahexaynediyl)diiron complex [14]. A recent remarkable work concerns sp C-chains surrounded by a double helix consisting of sp³ C-atoms [12g].

Linear C-chain species and nanotubes have attracted attention for a couple of years [15]. Carbon nanotubes represent very attractive systems in the area of material science. In connection with interest in C-chains, attention should also be paid to fullerenes and soot formation [16][17]. Stick-like silicate material with nanodomains of alternating $C{=}C$ and $C{\equiv}C$ bonds attracts attention in connection with optoelectronic devices [18].

Carbon-rich acetylenic systems play a distinguished role when designing elements and units in supramolecular and medicinal chemistry [19]. Related ideas represent a driving force in connection with molecular wires and devices [3a][20]. Extensive attention has been paid to the synthesis of cyclic homoconjugated oligodiacetylenes (the so-called 'exploded' pericyclynes). Some of these systems could act as precursors for the preparation of C-rich cage molecules: the most attractive of them is, perhaps, a hydrocarbon possessing adamantane-type structure in which $C-C$ bonds are replaced by the $C{\equiv}C-C{\equiv}C$ units. Transannular interactions in such a system would be of special interest [21]. Systems having two chains in a cycle consisting of eight $C{\equiv}C$ bonds, remarkable [12.12]paracyclophanedodecaynes, represent precursors of C_{36}^- carbon clusters [22]. In the near future, more attention might be paid to partial substitution of C [23] in $C{\equiv}C$ chains by silicon, which could be accompanied by desirable modification ('tuning') of electronic properties of those systems.

Electronic structure, geometry, and electronic spectra of simple cumulenes and azacumulenium cations were studied semi-empirically [24]. An extensive set of acetylenes and of acyclic and cyclic cumulenes was investigated in terms of non-empirical *H. F.* and semi-empirical SCF methods [25]; special attention was paid to highly strained systems.

Calculations. – All calculations in this paper were performed by means of the Gaussian98 program package, which permits to exploit different levels of including electron correlation [26]. The MP2, MP4 [27], and CCSD(T) [28] models were used with species having a small number of C-atoms, the *H. F.* and DFT (B3P86 and B3LYP) methods were used in all other cases [29]. Several correlation-consistent gaussian basis sets of atomic orbitals were used here; they ranged from valence double-zeta (cc-pVDZ) to valence quintuple-zeta (cc-pV5Z). With some small systems, also augmented basis sets were used (aug-cc-pVXZ). The pseudopotential SDD bases – the Stuttgart/Dresden ECPs – were used in calculations concerning Si, Ge, I, and Pt derivatives [30].

Results and Discussion. – *Energy Calculations.* Results of energy calculations for acetylenes **1** – **6** and cumulenes **7** – **12** are presented in *Table 1.*

It was shown in our previous work [1] that plots of the total *H. F.* energies and of energies including various levels of correction for electron correlation against the reciprocal values of the total number of atomic functions, $1/n$, permit to obtain good estimates of energies for infinite basis sets on the basis of extrapolation. (Other extrapolation procedures are quoted in [1].) In the paper cited, this extrapolation procedure was used for atoms, diatomics (and H_2O), and for very simple *Van der Waals* dimers. Extension into the realm of polyatomic organic molecules is topical. The energy plots presented here concern ethylene, acetylene, and propa-1,2-diene (*Fig. 1*). The reason why extrapolations with polyatomic species are always based on a small number of points is due to the fact that only the TZ and QZ basis sets, and their augmented versions offer reliable values for extrapolations (the DZ basis sets are, in general, not good enough, and the quintuply-zeta basis sets are too demanding for polyatomic molecules). Therefore, four points are usually at our disposal for extrapolation. When using the least-squares procedure for extrapolations, we add, as a constraint, a common limit for $1/n = 0$ for the both the standard and the augmented basis sets. Being interested in relatively extensive systems, we adopted for our calculations also a procedure based on the density functional theory (DFT). The *E vs.* $1/n$ plots assume the same character as those for more-rigorous types of calculations. Obviously, however, the location of the plots for DFT energies – significantly below the MP4 plots – does not have any physical significance. It is very probably a consequence of empirical characteristics included in those calculations. The situation is also analogous to the H_2O molecule studied previously; the DFT plots are added in *Fig. 2* to our former calculations [1]. When using the DFT method, one is interested in energy differences, not in absolute energy values.
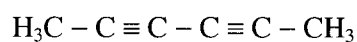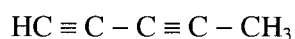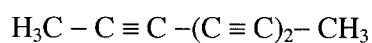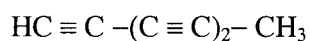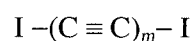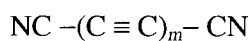
Two additional comments are worth mentioning. The first one concerns the fact that the linear dependences between total energies obtained by various procedures:

$$H-(C\equiv C)_m-H \qquad\qquad H_2C=(C)_m=CH_2$$
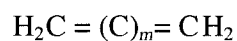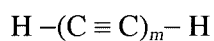
$D_{\infty h}$

	m
1	1
2	2
3	3
4	4
5	5
6	6

	m	
7	0	D_{2h}
8	1	D_{2d}
9	2	D_{2h}
10	3	D_{2d}
11	4	D_{2h}
12	5	D_{2d}

$$HC\equiv C-C\equiv C-CH_3 \qquad\qquad H_3C-C\equiv C-C\equiv C-CH_3$$

13 **14**

$$HC\equiv C-(C\equiv C)_2-CH_3 \qquad\qquad H_3C-C\equiv C-(C\equiv C)_2-CH_3$$

15 **16**

$$NC-(C\equiv C)_m-CN \qquad\qquad I-(C\equiv C)_m-I$$

	m
17	0
18	1
19	4

	m
20	1
21	3

$$E^N = a + bE \qquad\qquad (1)$$

(N in *Eqn. 1* stands for *H. F.*, MP2, MP4, CCSD(T), resp.) and the total DFT energy are very close, and the respective correlation coefficients assume values that approach unity. The situation with acetylenes is a good prototype; constants a and b together with correlation coefficients are summarized in *Table 2*. This result suggests that any of all these energies may be used for obtaining energy changes ΔE of comparable quality.

Our second comment concerns plots of total *H. F.* energies *vs.* $1/n$ for acetylene through pentaacetylene. The slopes of these plots show significant dependence on the size of the system. The calculated slopes for systems **1** through **5** amounts to 0.81, 3.0, 6.2, 10.6, and 16.1 a.u., respectively. It turns out, however, that the error on a percentage basis of the quadruply-zeta *H. F.* total energies (H. F./cc-pVQZ) with respect to the

Table 1. *Total Energies* E *[E$_a$] for Species* **1** – **12**, *Total Number* n *of Atomic Functions in the Basis Set and Extrapolated Energies for 1/*n → *0*

Method and basis set	n	$1/n$	$E\,[E_a]$	Limit for $1/n \to 0$
C$_2$H$_2$ (**1**):				
H. F./cc-pVDZ	38	0.02632	− 76.82604	− 76.85996
H. F./cc-pVTZ	88	0.01136	− 76.85062	
H. F./cc-pVQZ	170	0.00588	− 76.85573	
H. F./cc-pV5Z	292	0.00342	− 76.85684	
H. F./aug-cc-pVDZ	64	0.01562	− 76.82873	− 76.86015
H. F./aug-cc-pVTZ	138	0.00725	− 76.85138	
H. F./aug-cc-pVQZ	252	0.00397	− 76.85587	
MP2/cc-pVDZ	38	0.02632	− 77.08268	− 77.20708
MP2/cc-pVTZ	88	0.01136	− 77.15920	
MP2/cc-pVQZ	170	0.00588	− 77.18347	
MP2/cc-pV5Z	292	0.00342	− 77.19206	
MP2/aug-cc-pVDZ	64	0.01562	− 77.09300	− 77.20775
MP2/aug-cc-pVTZ	138	0.00725	− 77.16406	
MP2/aug-cc-pVQZ	252	0.00397	− 77.18574	
MP4/cc-pVDZ	38	0.02632	− 77.11059	− 77.23508
MP4/cc-pVTZ	88	0.01136	− 77.18925	
MP4/cc-pVQZ	170	0.00588	− 77.21136	
MP4/aug-cc-pVDZ	64	0.01562	− 77.12139	− 77.23523
MP4/aug-cc-pVTZ	138	0.00725	− 77.19386	
MP4/aug-cc-pVQZ	252	0.00397	− 77.21303	
CCSD(T)/cc-pVDZ	38	0.02632	− 77.11087	− 77.23257
CCSD(T)/cc-pVTZ	88	0.01136	− 77.18765	
CCSD(T)/cc-pVQZ	170	0.00588	− 77.20932	
CCSD(T)/aug-cc-pVDZ	64	0.01562	− 77.12138	− 77.23273
CCSD(T)/aug-cc-pVTZ	138	0.00725	− 77.19220	
CCSD(T)/aug-cc-pVQZ	252	0.00397	− 77.21100	
B3P86/cc-pVDZ	38	0.02632	− 77.57805	− 77.61646
B3P86/cc-pVTZ	88	0.01136	− 77.60495	
B3P86/cc-pVQZ	170	0.00588	− 77.61050	
B3P86/aug-cc-pVDZ	64	0.01562	− 77.58180	− 77.61685
B3P86/aug-cc-pVTZ	138	0.00725	− 77.60567	
B3P86/aug-cc-pVQZ	252	0.00397	− 77.61073	
C$_4$H$_2$ (**2**):				
H. F./cc-pVDZ	66	0.01515	− 152.50981	− 152.57428
H. F./cc-pVTZ	148	0.00676	− 152.55400	
H. F./cc-pVQZ	280	0.00357	− 152.56356	
H. F./aug-cc-pVDZ	110	0.00909	− 152.51391	− 152.57453
H. F./aug-cc-pVTZ	230	0.00435	− 152.55524	
H. F./aug-cc-pVQZ	412	0.00243	− 152.56376	
C$_6$H$_2$ (**3**):				
H. F./cc-pVDZ	94	0.01064	− 228.19470	− 228.28807
H. F./cc-pVTZ	208	0.00481	− 228.25824	
H. F./cc-pVQZ	390	0.00256	− 228.27216	
C$_8$H$_2$ (**4**)				
H. F./cc-pVDZ	122	0.00820	− 303.87971	− 304.00206
H. F./cc-pVTZ	268	0.00373	− 303.96256	
H. F./cc-pVQZ	500	0.00200	− 303.98089	
C$_{10}$H$_2$ (**5**)				
H. F./cc-pVDZ	150	0.00667	− 379.56473	− 379.71603
H. F./cc-pVTZ	328	0.00305	− 379.66688	
H. F./cc-pVQZ	610	0.00164	− 379.68961	

Table 1 (cont.)

C$_{12}$H$_2$ (**6**)				
H. F./cc-pVDZ	178	0.00562	– 455.24972	–
H. F./cc-pVTZ	388	0.00258	– 455.37118	
C$_2$H$_4$ (**7**):				
H. F./cc-pVDZ	48	0.02083	– 78.04017	– 78.07515
H. F./cc-pVTZ	116	0.00862	– 78.06442	
H. F./cc-pVQZ	230	0.00435	– 78.06974	
H. F./aug-cc-pVDZ	82	0.01220	– 78.04371	– 78.07546
H. F./aug-cc-pVTZ	184	0.00543	– 78.06525	
H. F./aug-cc-pVQZ	344	0.00291	– 78.07000	
MP2/cc-pVDZ	48	0.02083	– 78.31530	– 78.45172
MP2/cc-pVTZ	116	0.00862	– 78.39931	
MP2/cc-pVQZ	230	0.00435	– 78.42528	
MP2/aug-cc-pVDZ	82	0.01220	– 78.32892	– 78.45433
MP2/aug-cc-pVTZ	184	0.00543	– 78.40453	
MP2/aug-cc-pVQZ	344	0.00291	– 78.42769	
MP4/cc-pVDZ	48	0.02083	– 78.35358	– 78.48508
MP4/cc-pVTZ	116	0.00862	– 78.43816	
MP4/cc-pVQZ	230	0.00435	– 78.46141	
MP4/aug-cc-pVDZ	82	0.01220	– 78.36790	–
MP4/aug-cc-pVTZ	184	0.00543	– 78.44319	
B3P86/cc-pVDZ	48	0.02083	– 78.87868	– 78.91812
B3P86/cc-pVTZ	116	0.00862	– 78.90650	
B3P86/cc-pVQZ	230	0.00435	– 78.91226	
B3P86/aug-cc-pVDZ	82	0.01220	– 78.88388	– 78.91880
B3P86/ag-cc-pVTZ	184	0.00543	– 78.90715	
B3P86/aug-cc-pVQZ	244	0.00291	– 78.91256	
C$_3$H$_4$ (**8**):				
H. F./cc-pVDZ	62	0.01613	– 115.87262	– 115.92188
H. F./cc-pVTZ	146	0.00685	– 115.90636	
H. F./cc-pVQZ	285	0.00351	– 115.91393	
H. F./aug-cc-pVDZ	105	0.00952	– 115.87691	– 115.92212
H. F./aug-cc-pVTZ	230	0.00435	– 115.90756	
H. F./aug-cc-pVQZ	424	0.00236	– 115.91422	
MP2/cc-pVDZ	62	0.01613	– 116.26495	– 116.46507
MP2/cc-pVTZ	146	0.00685	– 116.38264	
MP2/cc-pVQZ	285	0.00351	– 116.41997	
MP2/aug-cc-pVDZ	105	0.00952	– 116.28291	– 116.47327
MP2/aug-cc-pVTZ	230	0.00435	– 116.39069	
MP2/aug-cc-pVQZ	424	0.00236	– 116.42353	
MP4/cc-pVDZ	62	0.01613	– 116.31442	–
MP4/cc-pVTZ	146	0.00685	– 116.43376	
MP4/aug-cc-pVDZ	105	0.00952	– 116.33324	–
MP4/aug-cc-pVTZ	230	0.00435	– 116.44153	
B3P86/cc-pVTZ	146	0.00685	– 117.09438	– 117.11134
B3P86/cc-pVQZ	285	0.00351	– 117.10265	
B3P86/aug-cc-pVTZ	230	0.00435	– 117.09543	– 117.11213
B3P86/aug-cc-pVQZ	424	0.00236	– 117.10307	
C$_4$H$_4$ (**9**):				
H. F./cc-pVTZ	176	0.00568	– 153.74730	– 153.76755
H. F./cc-pVQZ	340	0.00294	– 153.75707	
B3P86/cc/pVTZ	176	0.00568	– 155.28389	

Table 1 (cont.)

C$_5$H$_4$ (**10**):				
H. F./cc-pVTZ	206	0.00485	$-$ 191.59134	$-$ 191.61623
H. F./cc-pVQZ	395	0.00253	$-$ 191.60325	
B3P86/cc-pVTZ	206	0.00485	$-$ 193.47730	
C$_6$H$_4$ (**11**):				
H. F./cc-pVTZ	236	0.00424	$-$ 229.43471	$-$ 229.46428
H. F./cc-pVQZ	450	0.00222	$-$ 229.44877	
B3P86/cc-pVTZ	236	0.00424	$-$ 231.67056	
C$_7$H$_4$ (**12**)				
H. F./cc-pVTZ	266	0.00376	$-$ 267.27934	$-$
B3P86/cc-pVTZ	266	0.00376	$-$ 269.86569	
C$_8$H$_4$:				
H. F./cc-pVTZ	296	0.0338	$-$ 305.12353	$-$

Table 2. *Constants* a *and* b *of* Eqn. 1 *for Acetylene* (*r* is correlation coefficient; the number of points in all correlations amounts to 7)

N	*a* [a.u.]	*b*	*r*
H.F.	$-$ 7.2879	0.8964	1.000
MP2	169.1433	3.1739	0.997
MP4	169.6848	3.1812	0.998
CCSD(T)	164.0837	3.1090	0.998

extrapolated energy values (for $1/n = 0$) is nearly identical for the whole set of acetylenes and is equal to 0.007%.

Let us deal now with dimerization energies. It is appropriate to mention that DFT describes correctly H$_2$O dimerization, which had been studied previously [1]:

$$2 \, H_2O \rightleftharpoons (H_2O)_2, \, \Delta E \tag{2}$$

It has been shown [31] that it is always desirable to correct for the extension of the basis-set when passing from a monomer to a dimer, *i.e.,* to include the basis-set superposition error (BSSE). *Fig. 2, a*, shows that there is reasonable agreement between the ΔE of the H$_2$O dimerization (*Eqn. 2*) obtained by the DFT procedure and extrapolated MP2 value [1].

A process represented by *Eqn. 3* in which we are interested in this study is acetylene dimerization studied years ago [32]. Either of the two molecules involved in **22** can act as a proton donor; the structure of the *Eyring*-activated complex separating the two equivalent minima is represented by **23**.

Fig. 2, b and *c* show that the extrapolation scheme leads to ΔE of the equilibrium acetylene dimerization (*Eqn. 3*), $\Delta E^{\pm}$ values of the isomerization process (in which the role of the acetylene subunits in **22** is interchanged *via* activated complex **23**), which are in good agreement with previously obtained theoretical values [32].

Energy Characteristics: Heats of Formation, Ionization Potentials, and Electron Affinities. Experimental values from the literature [33] and calculated values are
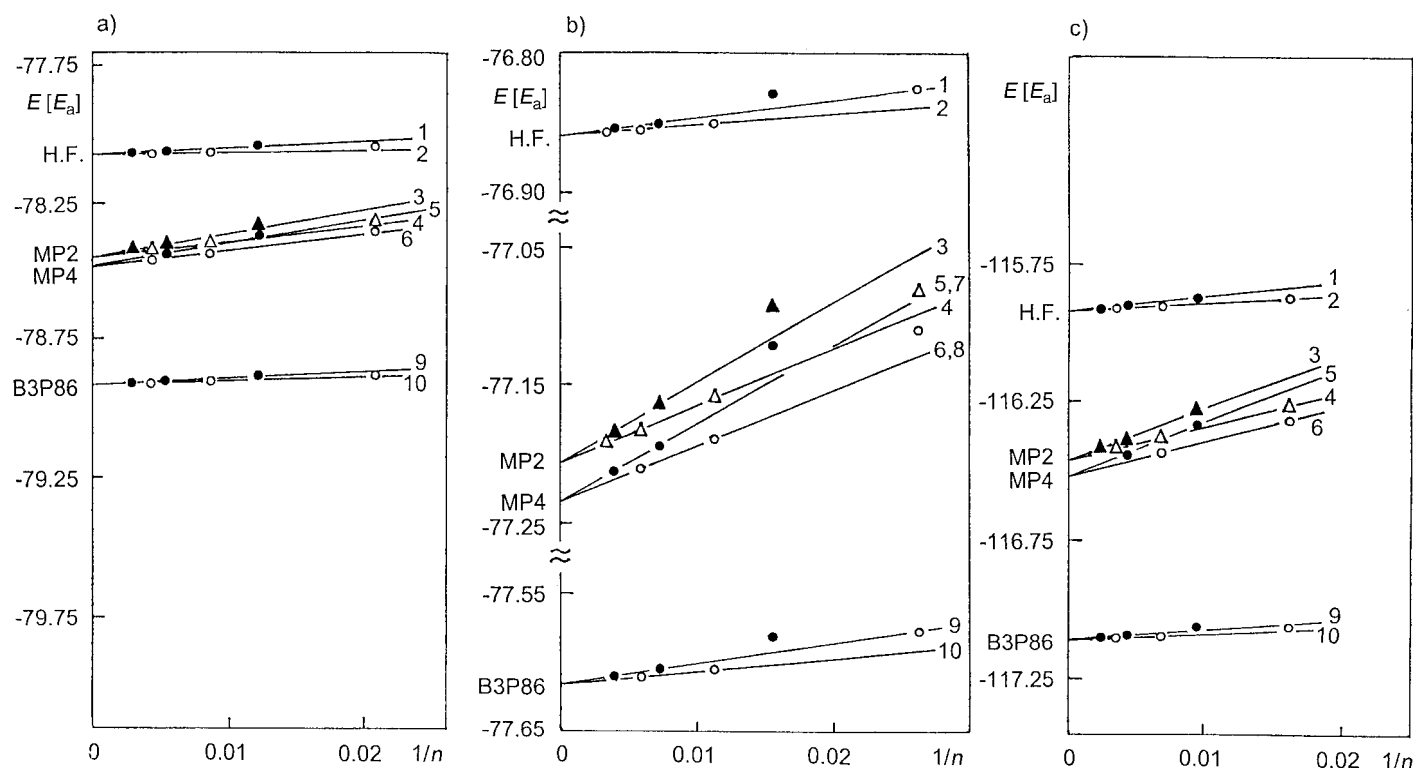
Fig. 1. *Total energies* E *[E$_a$] of* a) *ethylene,* b) *acetylene, and* c) *allene (propa-1,2-diene) calculated at* H. F., *MP2, MP4, CCSD(T), and DFT levels plotted against reciprocal values 1/*n *of number of functions in the respective basis set.* Designation: *1, H. F.*/aug-cc-pVXZ; *2, H. F.*/cc-pVXZ; *3,* MP2/aug-cc-pVXZ; *4,* MP2/cc-pVXZ; *5,* MP4/aug-cc-pVXZ; *6,* MP4/cc-pVXZ; *7,* CCSD(T)/aug-cc-pVXZ; *8,* CCSD(T)/cc-pVXZ; *9,* B3P86/aug-cc-pVXZ; *10,* B3P86/cc-pVXZ.
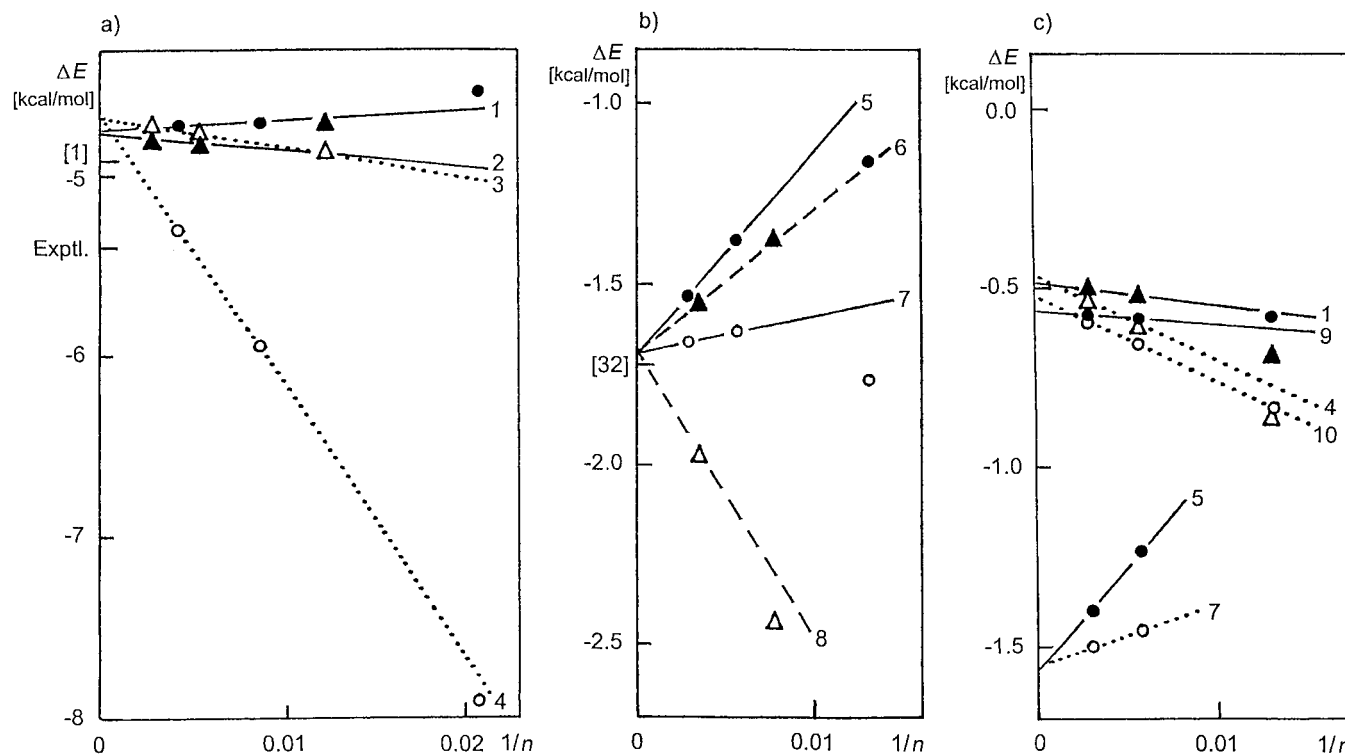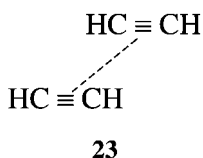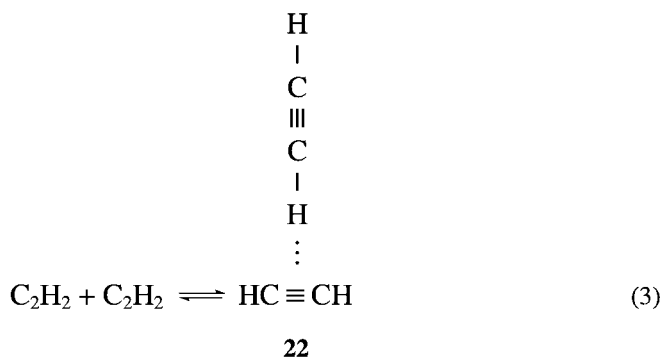
Fig. 2. *Calculated energy changes* ΔE [kcal/mol] *accompanying* a) H_2O, b) *acetylene dimerization, and* c) *connected with formation of the* Eyring *activated complex* **23** *plotted against reciprocal values* $1/n$ *of number of functions in the respective basis set.* Designation: *1*, B3P86/cc-pVXZ, BSSE; *2*, B3P86/aug-cc-pVXZ, BSSE; *3*, B3P86/aug-cc-pVXZ; *4*, B3P86/cc-pVXZ; *5*, MP2/cc-pVXZ, BSSE; *6*, MP2/aug-cc-pVXZ, BSSE; *7*, MP2/cc-pVXZ; *8*, MP2/aug-cc-pVXZ; *9*, *H. F.*/cc-pVXZ, BSSE; *10*, *H. F.*/cc-pVXZ.

$$\begin{array}{c} H \\ | \\ C \\ ||| \\ C \\ | \\ H \\ \vdots \end{array}$$

$$C_2H_2 + C_2H_2 \;\rightleftharpoons\; HC \equiv CH \qquad\qquad (3)$$

22

$$HC \equiv CH$$
$$HC \equiv CH$$

23

summarized in *Table 3*, and *Figs. 3* and *4*. Calculated data based on the DFT theory offer reliable estimates of relative values of all characteristics.

In case of heats of formation, *H. F.* data (in contrast to DFT data) are not able to reproduce the experiment. MP2 and CCSD(T) values fit, in general, experimental values satisfactorily. It has to be mentioned that experimental ΔH_f° values are reliable for only the first two lowest members; the remaining data represent only good estimates.

Koopmans theorem combined with *H. F.* orbital energies for the highest occupied and the lowest virtual orbitals permits obtaining theoretical estimates for vertical ionization potentials and electron affinities. *H. F.* Values reproduce the experiment satisfactorily; DFT (B3P86 and B3LYP) are shifted in absolute values but are suitable for correlations. It has to be added, however, that the *Koopmans* theorem is for DFT not valid and, therefore, using DFT characteristics has a purely empirical character. From *Fig. 4*, it is seen that the set of cumulenes forms two distinct subgroups belonging to D_{2h} and D_{2d} symmetry groups, having an even and odd number of C-atoms, respectively. This is understandable, because a cumulene having an even number of the C-atoms is, within the framework of π-electron theory in the first approximation, equivalent to the next nearest neighbor having one C-atom more.

Geometric Structure. Calculations for a few basis sets of increasing size are, in general, suitable for obtaining structural features for infinite basis sets. This is meaningful if very accurate X-ray data were available, which is not the case with the systems under study. Moreover, it turns out that, with the systems under study, the geometric data for the TZ a QZ basis sets are practically identical, so that extrapolation, in this case, is not topical.

By inspection of calculated bond lengths, it is seen that $C-C$ and $C\equiv C$ bonds of acetylenes and $C=C$ bonds of cumulenes converge rather rapidly to limiting values for

Table 3. *Heats of Formation*, ΔH_f, *Ionization Potentials* I, *and Electron Affinities* A *of Acetylenes and Cumulenes.* ΔH_f *in kcal/mol, I and A in eV.*

Molecule	ΔH_f exper.[a]	calc.[b]	calc.[c]	calc.[d]	exper.[a]	calc.[b]	calc.[c]	I calc.[e]	calc.[f]	A calc.[f]
Acetylenes										
1	54.5 ± 0.25 54.7	45.42	57.28	56.67	11.4 ± 0.02 11.4[g]	8.76	8.14	11.10	11.32	4.15
2	105	89.34	111.95	104.13	10.18 ± 0.03 10.16[g]	8.05	7.43	9.99	10.30	3.09
3	(155)	130.86	164.94	–	(9.50) 9.51[g]	7.68	7.06	–	9.79	2.16
4	(207)	–	216.87	–	(9.09) (9.06)[g,h]	7.45	6.83	–	9.50	1.58
5	–	–	–	–	–	–	–	–	9.32	1.19
6	–	–	–	–	–	–	–	–	9.18[i]	0.93[i]
Cumulenes										
7	12.5 ± 0.02 14.5	– 2.30	15.34	24.66	10.507 ± 0.004	8.25	7.63	10.25	10.38	3.58
8	45.6 ± 0.02 47.7	23.10	46.52	56.07	9.69 ± 0.01	8.07	7.47	10.27	10.36	3.44
9	(83)	48.11	77.26	–	(9.15)	7.47	6.85	–	9.21	2.20
10	(115)	70.36	105.28	–	(8.67)	7.36	6.75	–	9.18	2.31
11	–	92.94	133.43	–	–	7.09	6.47	–	8.57	1.02
12	–	114.33	160.41	–	–	7.02	6.40		8.53	1.29
[i]	–	–	–	–	–	–			8.15[i]	1.28[i]

[a]) Experimental values taken from *Lias et al.* [33]. Values in parentheses are less reliable than the other data.
[b]) B3P86/cc-pVTZ. [c]) B3LYP/cc-pVTZ. [d]) MP2/cc-pVTZ. [e]) MP2/cc-pVTZ. [f]) *H. F.*/cc-pVQZ. [g]) *Kloster-Jensen*. [h]) Extrapolated on the basis of value in [g]. [i]) Cumulene with eight C-atoms. [j]) *H. F.*/cc-pVTZ.

infinite linear and cyclic forms of acetylenes and cumulenes. When plotting calculated terminal C,C bond lengths (*H. F.*/cc-pVTZ) in acetylenes against the reciprocal number of C-atoms (or, equivalently, the number of C≡C bonds), linear dependence results. This dependence is slightly split into two subclasses corresponding to acetylenes possessing in the middle of the molecule the ≡C−C≡ or −C≡C− groups. These two dependencies converge to a common limit, which amounts to 1.190 Å for the C≡C bond and 1.366 Å for the C−C bond. This is in fair agreement with recent estimates for infinite acetylene by *Toto et al.* [34], which were 1.196 – 1.203 Å and 1.357 – 1.373 Å, respectively. An analogous extrapolation with cumulenes leads to a uniform value of 1.297 and 1.301 Å for D_{2h} and D_{2d} cumulenes, respectively.

For many chemists, species like acetylenes and cumulenes present strictly linear, rather rigid systems, which, however, is not the case. From this point of view, recent results of structural analysis of relatively long acetylenes and cumulenes are not too surprising. It was found by X-ray analysis that long polyacetylenes capped by organometalics are not linear [12c, d] [14]. On the other hand, we have shown that all the eigenvalues of the Hessians of linear polyacetylenes, including pentaacetylene, are positive. To be sure that the linear form represents the only minimum on the potential-energy surface, the geometry optimization of polyacetylenes was started with a bent
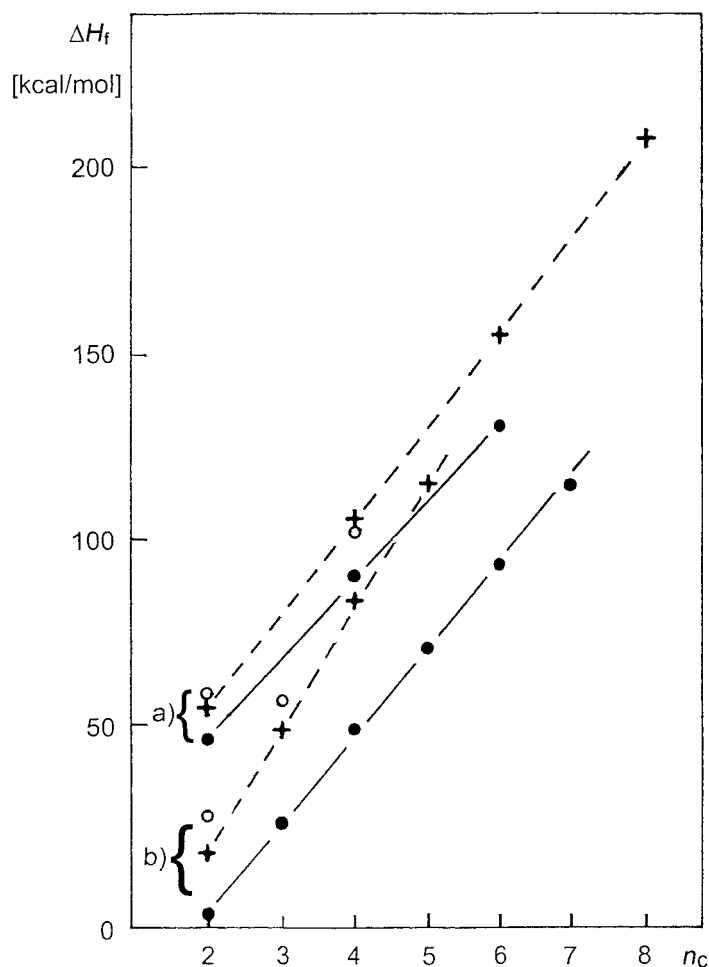
Fig. 3. *Experimental and calculated heats of formation plotted against the number of C-atoms* a) *in acetylenes and* b) *cumulenes*. Designation: + : experimental values, ●: B3P86/cc-pVTZ values, ○ MP2/cc-pVTZ values (*cf. Table 3*).

structure possessing all the C−C−C angles equal 177°. Also this structure converged slowly to a linear one.

In crystals of polyacetylenes capped by organometallics, interaction between the transition-metal atom (M) and the neighboring acetylenic chain could play a role. To estimate the influence of this interaction, model systems consisting of acetylene or triacetylene with Ni- or Pt-atom were investigated. A metal atom was located either in the long axis **24** or in the axis located perpendicular to the long axis **25**. The distance between the metal atom and the H-atom (in the former case) was equal to 2, 3, and 4 Å; in the latter case, the same distances concerned the gap between the metal atom and the acetylene center. These distances were kept constant during the geometry optimization. In the linear arrangement, the influence of the metal atom on the acetylene
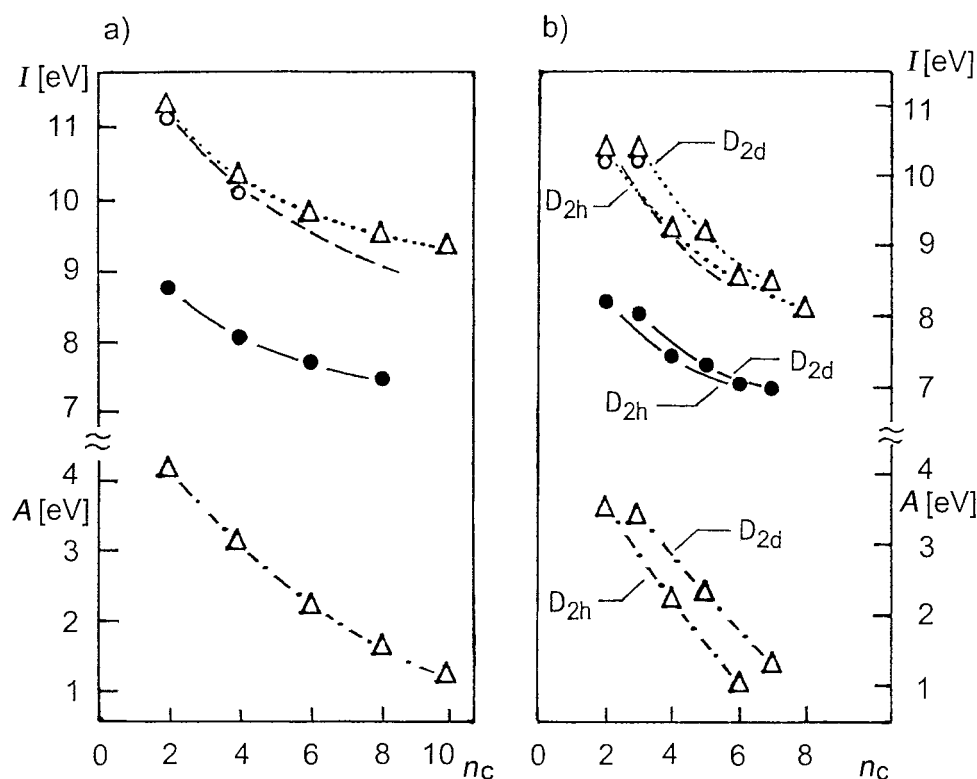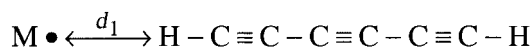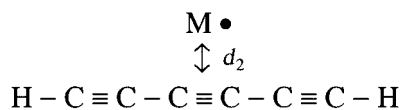
Fig. 4. *Experimental and calculated ionization potential* I *and calculated electron affinities* A *plotted against the number of C-atoms in* a) *acetylenes and* b) *cumulenes.* Designation: —: plots based on experimental values, ●: B3P86/cc-pVTZ, △: *H. F.*/cc-pVQZ, ○: MP2/cc-pVTZ.

geometry was negligible. In the perpendicular model with $d_2 = 3$ Å, the deviation from linearity amounts to *ca.* 3°, which is near the experimentally observed deviations from linearity in long acetylenes. However, when $d_2 = 4$ Å, which seems to be much nearer to reality, the influence of the metal atom is nearly negligible. The plausibility of this consideration is supported by the structure elucidation of an Ir complex with substituted butatriene [13]. In this complex, the distance between the Ir-atom and the middle of the central C=C bond amounts to *ca.* 2.05 Å, and this has a dramatic influence on the geometry of the butatriene subunit: it is strongly bent with the C–C–C angles of *ca.* 144°.

An analysis of calculated IR spectra (harmonic approximation) led to another possibility of how to interpret the deviation from the linearity observed experimentally with long acetylenic chains. It turned out that the lowest-energy deformation vibration (its nature was ascertained by inspecting the respective eigenfunction) decreases dramatically when passing from acetylene to longer acetylenes. This is depicted in *Fig. 5* and is valid for both acetylenes and cumulenes. This means that these systems are getting significantly softer with the increasing number of C-atoms due to the lowest-energy deformation modes. The shape of those lowest-energy deformation eigenfunc-

$$M \bullet \xleftarrow{\hspace{0.3cm} d_1 \hspace{0.3cm}} H - C \equiv C - C \equiv C - C \equiv C - H$$

24

$$M \bullet$$
$$\updownarrow d_2$$
$$H - C \equiv C - C \equiv C - C \equiv C - H$$

25

tions is indicated in *Fig. 6*, and it is similar to that found for various capped polyacetylenes by X-ray analysis: bent rods and prolongated S-shape. We close this paragraph by mentioning that a detailed study of vibrational and electronic spectra will be published later. But it seems appropriate to indicate already here the capability of the *Wilson* matrix analysis on the basis of *H. F.* calculations (*H. F.*/cc-pVTZ): the illustration concerns a vibrational spectrum of acetylene (*Table 4*). It can be seen that the frequencies are reproduced semi-quantitatively, while intensities are, qualitatively speaking, correct. With respect to our interpretation of deviations of long chains from linearity, it is a positive feature that the calculated frequencies are shifted, with respect to the observed ones, to higher frequencies. It means that the dependence in *Fig. 5* represents an upper limit.

Table 4. *Vibrational Spectrum of Acetylene*

No.	Symmetry	v [cm^{-1}]		Intensity; calc.[a]		Intensity; obs.	
		calc.[a]	obs.[b]	IR [km/mol]	*Raman* [A^4/a.m.u.]	IR	*Raman*
1, 2	Π_g	808	612[c]	0	6	?	–
3, 4	Π_u	869	729[c]	110	0	?	–
5	σ_g[d]	2213	1974	0	89	0	vs
6	σ_u[e]	3555	3287	95	0	s	0
7	σ_g[f]	3673	3374	0	41	0	s

[a]) *H. F.*/cc-pVTZ. [b]) From [35]. [c]) From [36]. [d]) C≡C Stretch. [e]) ≡C−H Asymmetric mode. [f]) ≡C−H Symmetric mode.

Electron Distribution and Reactivity. Although the *Mulliken* population analysis suffers from various weaknesses, it is reliable enough to establish some pronounced features. With polyacetylenes, we find a high surplus of electron density at the terminal C-atoms (roughly speaking, 0.3 to 0.5 e), and a small lack of electrons at the remaining C- and H-atoms. With the latter, it amounts to *ca.* 0.05 e. This electron distribution suggests that all polyacetylene molecules represent prefabricates for the respective dianions; this is why acetylenes, although mere C-acids, reveal a relatively high acidity. It must be added that results of the population analysis are rather strongly dependent on the extent of the basis set used in the *H. F.* calculations.
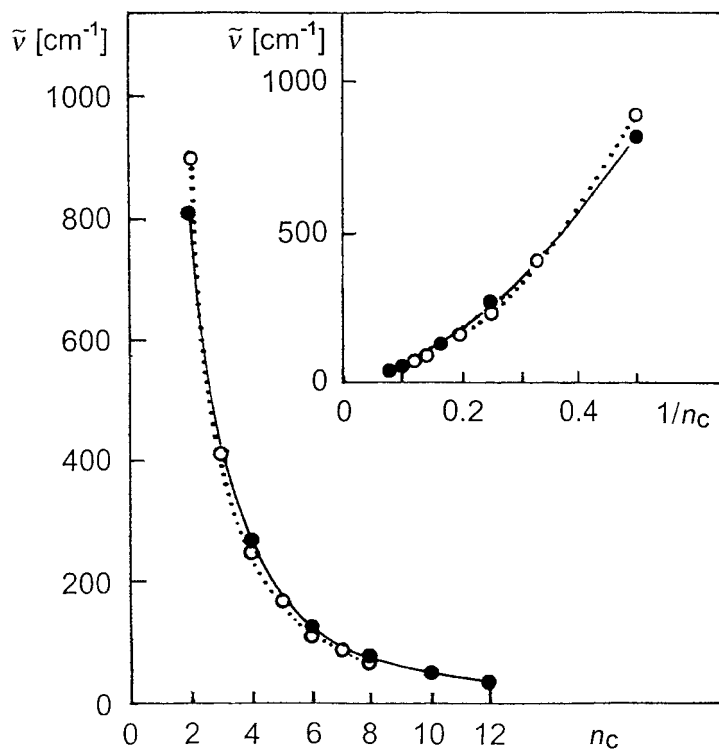
Fig. 5. *Dependence of the wave-number of the lowest-energy harmonic deformation mode* (*H. F.*/cc-pVTZ) *on the number of C-atoms in the chain,* n_c, *and on its reciprocal value,* $1/n_c$. Designation: —: acetylenes, ⋯: cumulenes.

Gas-phase energies of the two-step deprotonization (*Eqns. 4* and *5*) decrease significantly when passing from acetylene to triacetylene (*Table 5*). The energy difference between the first and third member of the series amounts to 24 kcal/mol. This agrees qualitatively with the experimental statement that the acidity of ethynyl-H-atom in polyacetylenes increases as the chain length is increased [8a] [37].
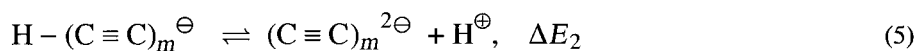
$$H - (C \equiv C)_m - H \; \rightleftharpoons \; H - (C \equiv C)_m{}^{\ominus} + H^{\oplus} \; , \quad \Delta E_1 \tag{4}$$

$$H - (C \equiv C)_m{}^{\ominus} \; \rightleftharpoons \; (C \equiv C)_m{}^{2\ominus} + H^{\oplus}, \quad \Delta E_2 \tag{5}$$
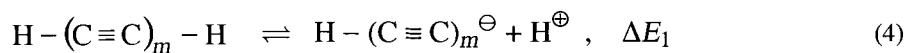
Table 5. *Two-Step Gas-Phase Dissociation of Acetylenes.* ΔE in kcal/mol; calculation *H. F.*/cc-pVTZ.

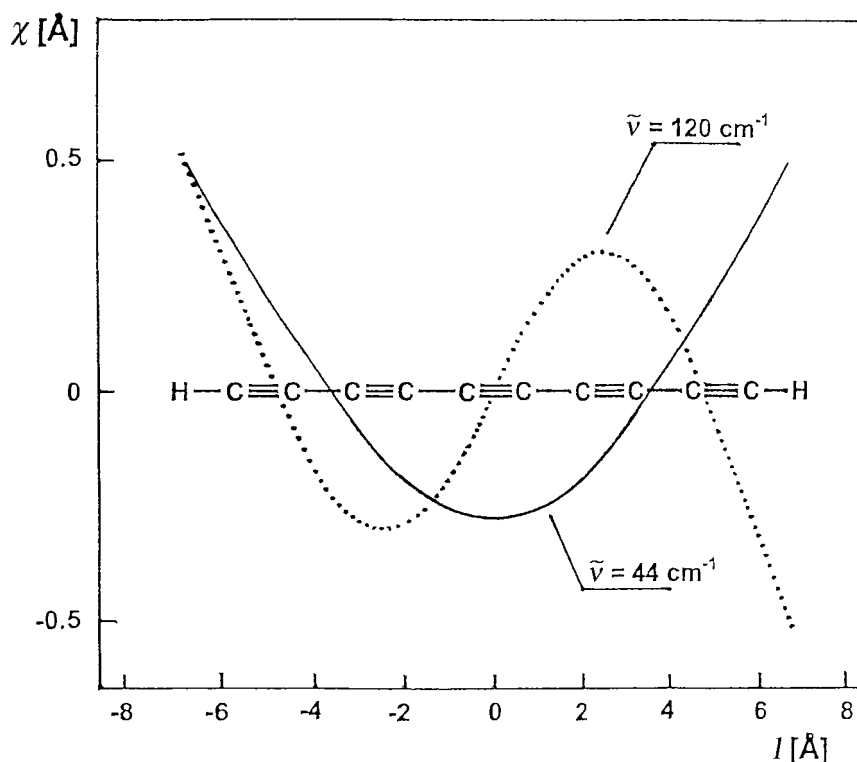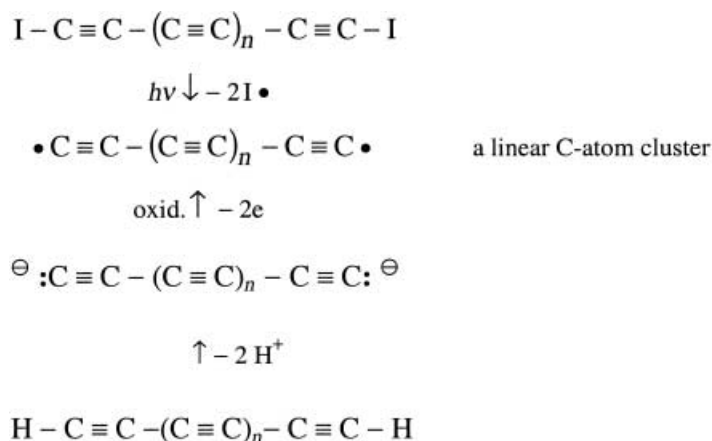| m in *Eqns. 4* and *5*	ΔE_1	ΔE_2
1	392	547
3	368	450

Fig. 6. *Graphical representation of vibrational wave function for the two lowest-energy deformation modes for pentacetylene* **5** *at the* H. F./*cc-pVTZ level*

A surplus of electron density at the terminal atoms is also observed with cumulenes. Also here, a slight difference between D_{2h} and D_{2d} systems is observed. In contrast to acetylenes, the negative charge is associated with the terminal C=C bond; the terminal C atom bears a higher electron surplus than its neighboring C-atom. We admit that we were surprised at the magnitude of electron surplus at the terminal C-atoms. Therefore, one should not expect that relatively high acidity will be a specific feature of acetylenes only; we consider it expedient to check the acidity of cumulenes experimentally.

In this connection, also processes leading to C-atom clusters should be mentioned. Polyacetylenes and derivatives thereof are potential precursors for the preparation of defined linear chains of sp C-atoms. A route starting from diiodo derivatives was discussed by *Gao* and *Goroff* [10a] for diiodo derivatives of **3** and **4**. It seems realistic to expect that this approach might be useful also with more-extensive systems. Another possibility exploits the acidity of polyacetylenes (which increases with the length of the system) and oxidation of the dianion formed. Electrochemical oxidation might be particularly useful for this purpose (*Scheme 1*). Let us mention that, recently, very long linear anionic chains (C_{70}^{2-}) were prepared from cage precursors by reduction with alkaline earth in liquid NH_3 [38]. Very probably, this type of process would be applicable to cages of different sizes.

Scheme 1

$$I-C\equiv C-(C\equiv C)_n -C\equiv C-I$$

$$hv \downarrow -2\,I\,\bullet$$

$$\bullet\,C\equiv C-(C\equiv C)_n -C\equiv C\,\bullet \qquad \text{a linear C-atom cluster}$$

$$\text{oxid.}\uparrow -2e$$

$$^{\ominus}:C\equiv C-(C\equiv C)_n -C\equiv C:^{\ominus}$$

$$\uparrow -2\,H^+$$

$$H-C\equiv C-(C\equiv C)_n -C\equiv C-H$$

In this section, also a note is appropriate concerning the use of C-rods (possibly terminated with heteroatoms) as semiconductive building elements for molecular devices. It seems possible and promising to use relatively short species (possessing $2-6$ C-atoms) as connecting elements; longer molecules might be less useful because of enhanced reactivity and significant vibrational softness. Insertion of benzene rings would make such connectors longer. In various situations of nanoscale electronics and photonics, inorganic semiconductor nanowires might be more promising. Moreover, *e.g.*, ZnO nanowires can function as UV nanolasers [39].

Derivatives and Hetero Analogues. Derivatives. Substitution of the terminal H-atoms in acetylenes enhances their chemical stability by keeping individual moieties farther apart. This is true with substituents like Me or halogen atoms. Iodine seems to be really efficient, mainly due to the volume of this atom.

When passing from diacetylene to its mono and dimethyl derivatives, an experimentally observed [6b] shift of the first ionization potential amounts to 0.5 and 1.0 eV, which is in good agreement with calculated shifts for transitions from **2** to **13** and **14**, respectively. The situation with **3** and its mono and dimethyl derivatives, **15** and **16**, is analogous.

Monosubstitution by halogen atoms diminishes the first ionization potential by 0.3, 0.4, and 0.75 eV for Cl, Br, and I, respectively [6b]. Also these shifts are correctly reproduced by *H. F.* calculations. As an illustration, let us mention that passing from diacetylene **2** to diiododiacetylene manifests itself by a decrease of the ionization potential by 1.25 eV; the calculated shift (*H. F.*/SDD) amounts to 0.86 eV.

The calculated bond lengths in Å (*H. F.*/SDD; basis set for I with pseudo-potential) in diiodotriacetylene agree with those observed experimentally: C(1)−I, 2.01, 1.96; C(1)−C(2), 1.20, 1.20; C(2)−C(3), 1.38, 1.38; C(3)−C(4), 1.20, 1.20.

Passage from cumulenes to tetrafluorocumulenes is worth mentioning: ionization potentials increase, electron affinities decrease, and reactivity in general increases. Features of geometry are outlined in *Fig. 7*. The lowest-energy deformation modes are

shifted significantly to smaller values. Let us add that this is true with all the derivatives and hetero analogues under study except α,ω-dicyanopolyacetylenes (*vide infra*).
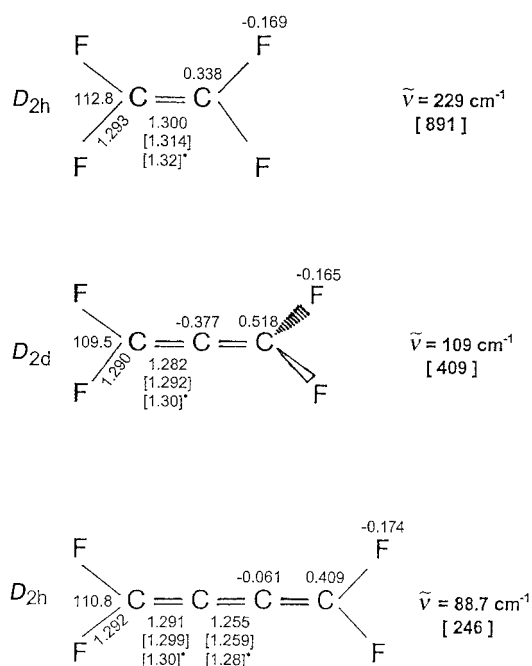

Fig. 7. *Calculated bond lengths* [Å] *and angles* [°] *for the first three perfluorocumulenes at the* H. F.*/cc-pVTZ level.* The lowest – energy deformation modes are presented (in parentheses the corresponding geometry values and wave-numbers for the parent cumulenes are given); *: experimental bond lengths for the parent cumulenes are taken from [40]. *Mulliken* atom populations are ascribed to the respective atoms.

Hetero Analogues. Isoelectronic substitution (with respect to the valence electrons) of the terminal CH group leads to the system of type **26** or **27**.
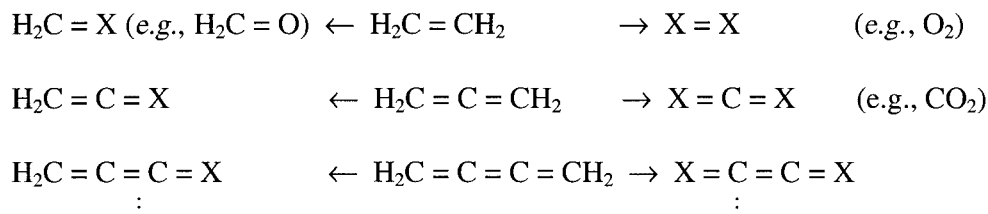
In the case of **27**, in principle, any C atom in the chain can be substituted, *i.e.,* not only the terminal one as indicated.

$$X \equiv C - (C \equiv C)_n - C \equiv X \qquad HY \equiv C - (C \equiv C)_n - C \equiv CH$$

26 X = N, or P   **27** Y = Si, or Ge
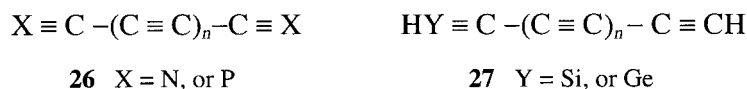
The α,ω-dicyano derivatives were intensively and systematically studied [11]. Here, we wish to briefly mention just one feature. These derivatives are the only ones that exhibit far-reaching similarity to the parent polyacetylenes. This concerns not only geometry and molecular characteristics but also vibrational features, particularly the lowest-energy deformation vibrations, which are, for the higher members of the both series, essentially identical. For diacetylene **2** to pentaacetylene **5**, and their N-analogues, the following *H.F.*/cc-pVTZ wave-numbers have been obtained: 259, 282; 121, 125; 69, 70, and 44, 45 cm^{-1}. All these deformation vibrations are allowed, and the intensity of the latter (*i.e.*, α,ω-dicyano derivatives) is by a factor of *ca.* 2 higher.

None of the four investigated Si and Ge analogues of diacetylene **2** exhibit minima on the *H. F.* potential surface; all represent first-order saddle points. Recent experimental successes indicate [23], however, that systems of type **27** might exist. No doubt, however, the systems of the type **27** studied here will not be very stable.

Also with cumulenes heteroanalogues having a substitution of C by Si, or Ge might exist. Much more experience is available with systems resulting from mono- or disubstitution of the terminal CH_2 groups by O, S, or NH (*Scheme 2*).

<div align="center">*Scheme 2*</div>

$$H_2C = X \ (e.g., \ H_2C = O) \ \leftarrow \ H_2C = CH_2 \qquad\qquad \rightarrow \ X = X \qquad\qquad (e.g., \ O_2)$$

$$H_2C = C = X \qquad\qquad \leftarrow \ H_2C = C = CH_2 \quad \rightarrow \ X = C = X \qquad (e.g., \ CO_2)$$

$$H_2C = C = C = X \qquad \leftarrow \ H_2C = C = C = CH_2 \ \rightarrow \ X = C = C = X$$
$$\vdots \qquad\qquad\qquad\qquad\qquad\qquad \vdots$$

Hetero analogues of cumulenes in which the terminal CH_2 groups are substituted by O, S, NH, respectively, are, from a formal point of view, topical in our context. In fact, however, lack of stability of these species precludes their extensive use as construction rods. The reason why these systems have attracted attention during the last 10 – 15 years is due to their tempting or even provocative electronic structure [41] [42], and also to the fact that some of them (or related systems) are obviously present in interstellar space. The first members of the series, $X=C=(C)_m=X$ (X = O, S, NH), $m = 0$, are well-known and stable. The situation is completely different with the next members, $X=C=C=X$ (X = O, S). It can be shown [41] on the basis of a correlation diagram (correlation of states of CX and C_2X_2) why these systems assume a triplet ground state, and why, particularly, the O derivative is energetically handicapped with respect to two CO molecules. It is worth mentioning that, at the MP2 and MP4 levels, the only localized stationary point on a singlet potential-energy surface is a saddle point. In contrast, the corresponding radical cation derived from C_2O_2 has a minimum on the doublet potential-energy surface; its structure is, however, not linear [43].

B3P86/cc-pVTZ Calculations for dicarbonyl systems **28 – 32** having one to five C-atoms indicate a clear split into two classes. Those having an odd (even) number of C-atoms (**28**, **30**, **32**, and **29**, **31**, resp.) possess a singlet (triplet) ground state. Clearly, the first member of this series, CO_2 **28**, belongs to it purely formally. The total energies of these systems form a strictly linear function of *m* (in formulas **28 – 32**). While ionization potentials of singlet species (8.78 and 7.97 eV for **30** and **32**, resp.) is significantly higher than those with triplet ground state (7.64 and 7.19 eV for **29** and **31**, resp.), electron affinities, *i.e.* reducibility of singlets are enhanced (− 2.56 and − 3.61 eV for **30** and **32**, resp.) with respect to triplets (1.26 and − 1.14 eV for **29** and **31**, resp.). Vibrational analysis of **28 – 32** indicates that all these systems possess lowest energy deformation vibration, which is smaller than that of the isoelectronic cumulenes, *i.e.*, these systems are softer.

It was shown by recent sophisticated calculations (MCSCF, MRCI), among other points [44], that the singlet state of C_2S_2 lies below the ground-state of the dissociation

product. Mass spectrometrical and theoretical studies have contributed significantly to the understanding of this area [45].

$$O = C(= C)_m = O$$
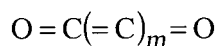
	m
28	0
29	1
30	2
31	3
32	4

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