ELECTRONIC SPECTRA OF CONJUGATED POLYYNES, CUMULENES AND RELATED SYSTEMS: A THEORETICAL STUDY

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Dedicated to Professor Josef Paldus, the master of theoretical chemistry, whose contribution is so profound that it will be deeply appreciated well into the future.

Electronic spectra of conjugated polyynes [$H(C\equiv C)_{nT}H$, nT = 1 to 7] and cumulenes [$H_2(C)_{nC}H_2$, nC = 1 to 9] were calculated by means of the time-dependent density functional theory (TD DFT) and, for a group of selected molecules, also by the symmetry-adapted cluster configuration interaction method (SAC-CI). A comparison was made between calculated and published experimental spectral data. It turned out that the TD DFT (with B3LYP) was a reliable tool for calculation of band positions in the longest-wavelength region. In the case of cumulenes, except allene, only data for alkyl and phenyl derivatives are available. The characteristics of cumulenes split into two distinctly separate classes, planar (with an even number of carbon atoms, D_{2h}) and non-planar (with an odd number of carbon atoms, D_{2d}). Special attention was paid to the influence of substituents of various types on the position of the first intensive bands of polyynes and polyenes. Plotting wavenumbers of these bands against the reciprocal number of the CC triple bonds (polyynes) or the CC double bonds (polyenes) lead to (partial) rectification and made the extrapolation to infinite chains easier. While the extrapolated value for infinite polyynes (and derivatives like dimethyl or dicyano) amounts to about 16 000 cm^{-1}, for anions and radical anions derived from the parent polyynes, the extrapolated value tends to significantly smaller values or possibly to zero. The situation with polyenes and their derivatives and heteroanalogues is similar; small deviations from zero with chains without significant bond alternation seem likely.

Keywords: Polyynes; Cumulenes; Electronic spectra; Quantum chemical calculations; *Ab initio* calculations; DFT; SAC-CI.

Electronically excited states do play a key role in photophysics, photochemistry, and in some parts of molecular biology. Molecular quantum mechanics offers several tools for describing the individual excited states be-

longing to various manifolds as well as transitions between them. About half a century ago, during the epoch of semiempirical methods, description of ground state[1] and excited state[2] properties was possible at a similar level of sophistication. It concerned the π-electron approximation, which was valuable for planar conjugated hydrocarbons and derivatives thereof. Since that time, due to the fundamental progress of methods of quantum chemistry and the revolutionary expansion of hardware, amazing achievements have been made for very different systems in the area of ground state properties and reactivity. In contrast, the situation in the realm of electronically excited states and interpretation of electronic spectra of polyatomic species is still less than satisfactory.

At present four or five procedures are available for studying electronic spectra, i.e., spectra in the visible, near UV and vacuum UV regions. The complete active space perturbation theory (the CASPT2 method) appears to be the most reliable[3], although it is not free of technical difficulties. Unfortunately, overcoming the complete active space self-consistent field procedure (CASSCF) is frequently not straightforward but is rather demanding. When dealing with extensive systems, the time-dependent density functional theory (TD DFT) (a single-reference based procedure) is attractive[4] but less accurate than the previous procedure and techniques we will mention later. Before doing that, let us add that significant progress has been recently made with DFT, which permits investigation of excited state hypersurfaces, i.e., the geometry of their stationary points and properties[5].

Recently, applicability of the multireference Møller–Plesset (MR-MP2) method[6] was studied and its performance compared with TD DFT and the approximate coupled cluster method with single and double excitations[7] (CC2). It turned out, with a set of 14 structurally different species that the MR-MP2 is superior to all the systems under study with respect to the two other procedures used.

Within the framework of the search for interstellar molecules, spectroscopic constants and other physical characteristics of cyanopolyynes and related systems were calculated[8]. These and related systems (e.g., $C_{2n+1}N$ radicals, monosilicon carbide, SiC_n, pure carbon chains) assume the cumulene character, which is associated with splitting data into two subgroups (vide infra).

Extensive experimental and theoretical studies have been carried out during the last few years in Maier's group[9]. Studied were several sets of systems (polyynes, heteroanalogues and derivatives thereof, radical anions and nonclassical species related to polyynes having a triplet ground state), possessing in some instances up to 26 carbon atoms. The species under investiga-

tion were generated by methods related to mass spectrometry and spectra were recorded in the gas phase or in neon matrices. Only papers dealing with long polyynes and anions thereof are directly related to the subject of this work. However, from a structural point of view, polyyne-like chains with odd number of carbon atoms, possessing H atoms at both the ends (i.e., the $HC_{2n+1}H$ systems) are noteworthy. They might be considered linear (triplet) carbenes substituted by polyyne chains. The first singlet vertical excitations of the $HC_{2n}H$ systems and the first triplet excitations of the $HC_{2n+1}H$ systems were calculated at the TD DFT level[10].

Due to our interest[11] in polyynes and cumulenes as potential elements for molecular machines, and as species potentially occurring in interstellar space, we have become interested in electronic spectra of these unsaturated hydrocarbons. A remarkably good performance of the DFT method (related to a CBS study[12] of a representative set of species) in comparison with methods ranging from the Hartree–Fock SCF to the CCSD(T) method prompted us to use the time-dependent DFT procedure for dealing with electronic spectra of polyynes and cumulenes. Moreover, we considered it expedient to carry out more sophisticated SAC-CI calculations[13] for a group of smaller molecules belonging to the main series of the molecules studied.

COMPUTATIONS

We used the Gaussian 03 program package[14] throughout. The ground states of studied molecules were optimized at SAC[13] and DFT[4] levels. In a few cases we tested electronic spectra for different exchange-correlation functionals as B3LYP, HCTH and PBE1PBE. The hybrid B3LYP functional is very popular, the asymptotically corrected HCTH functional yields significantly improved Rydberg excitation energies[15] and the hybrid PBE1PBE functional seems to be significantly less affected by errors of high-energy transitions than other hybrid functionals, as discussed in a paper by Adamo and Barone[16]. Otherwise, the electronic spectra were simulated using TD-B3LYP and with smaller molecules SAC-CI (SD-R) methods. All calculations were made in combination with the correlation consistent polarized valence n-zeta basis sets, aug-cc-pVnZ[17], with n = D (double), T (triple), Q (quadruple). The specific basis used is mentioned in the text. If we also performed computations with cc-pVQZ, we tried to extrapolate excitation energies to the complete basis set limit. Systematic calculations for polyynes (one to seven triple bonds) and cumulenes (up to nine carbon atoms) were performed with TD DFT (B3LYP) with augmented TZ basis sets.

The peak intensities in electronic spectra were represented by oscillator strength, *f*, that depends on the transition moment according to the formula, $f = (8\pi^2/3)(m_\mathrm{e} \nu/he^2)|{-}e\int \Psi_f^* r \Psi_i \, dr|^2$, where the symbols have their usual meaning. Moreover, the dimensionless oscillator strength is directly associated with the extinction coefficient, $\varepsilon(\tilde{\nu})$: $f \approx \int \varepsilon(\tilde{\nu}) \, d\tilde{\nu}$. This expression allowed us to fit Gauss (or Lorentz) curves in the case we chose the Gauss (or Lorentz) function for $\varepsilon(\tilde{\nu})$. In the present work we modeled electronic spectra with Gauss and Lorentz curves with equal weights; the half-width of peaks was adjusted to 3000 cm^{-1}.

RESULTS AND DISCUSSION

Before we begin comparing calculated and experimental spectral data for polyynes and cumulenes, it is desirable to be aware of changes of spectral data when passing from TD DFT to SAC-CI (Table I). In all instances this passing with all types of transitions brings about a significant hypsochromic shift of 0.3–1.5 eV. These differences become smaller with increasing size of the system. Substitution of the ≡CH grouping by ≡N (e.g., transition between HC≡CH and HC≡N, and between HC≡C–C≡CH and N≡C–C≡N) is related to a significant bathochromic shift which is in qualitative agreement with experiment (vide infra). Moreover, these calculations make possible estimates of band positions for the complete basis sets (CBS). It is known[12] that obtaining accurate theoretical values requires carrying out these extrapolations. Experience with calculated electronic transition energies is still very limited. The values obtained (Table I) suggest that the basis set effect is diminishing with increasing size of the system. With small systems passing from DZ to QZ, the basis set effect can reach values as high as 1 eV. In majority of instances it amounts to lower values of 0.1–0.2 eV. This passing brings about monotonic changes. In some instances, however, a curved shape occurs. On the basis of available experience it is hardly possible to make a reliable a priori prediction of the type of behavior. This is also the case with other physical characteristics[12]. Therefore, it is necessary to treat each molecule quite individually.

Another point deserves attention, namely the availability of various versions of the TD DFT procedure (Table II). In all instances the DFT excitation energies are by 1–2 eV smaller than the SAC-CI ones; the former values are nearer to experimental values. Passing from DZ to TZ basis sets is significant and changes of about 0.5 eV are not exceptional. This suggests that extrapolations to complete basis sets are desirable. There is fair agreement (except HCTH data for ethene) with excitation energies and intensities among the

The first two electronic transitions for selected small systems: Comparison of methods and basis sets

Molecule	Method	DZ		TZ		QZ	
		$\tilde{\nu}$	f	$\tilde{\nu}$	f	$\tilde{\nu}$	f
Ethene	TD-B3LYP	49 340	0.253	48 910	0.268	47 130	0.329
		59 860	0.019	57 010	0.030	57.140	0.028
	SAC-CI	70 770	0.457	67 920	0.445	66 580	0.430
		73 570	0.025	69 260	0.034	66 390	0.044
Buta-1,3-diene	TD-B3LYP	42 100	0.664	41 060	0.667	–	–
		56 040	0.003	54 770	0.006	–	–
	SAC-CI	55 340	0.851	52 800	0.839	–	–
		67 320	0.000	62 480	0.001	–	–
Ethyne	TD-B3LYP	72 200	0.006	69 160	0.014	66 170	0.033
		79 580	0.739	77 040	0.779	74 690	0.762
	SAC-CI	85 730	0.007	81 750	0.017	89 130	0.096
		98 940	1.215	93 570	1.115	90 550	0.502
Butadiyne	TD-B3LYP	62 810	0.001	61 800	0.004	–	–
		62 520	2.038	61 130	2.031	–	–
	SAC-CI	77 060	0.001	74 410	0.007	–	–
		77 590	2.307	73 971	2.451	–	–
Propadiene	TD-B3LYP	61 920	1.041	61 012	1.049	60 000	1.022
		65 140	0.001	61 530	0.006	58 600	0.012
	SAC-CI	71 910	1.399	69 330	1.320	67 525	1.225
		74 050	0.002	68 220	0.009	64 980	0.023
Buta-1,2,3-triene	TD-B3LYP	42 700	0.349	42 400	0.373	–	–
		63 990	0.019	61 100	0.029	–	–
	SAC-CI	48 480	0.281	46 160	0.523	–	–
		71 820	0.014	67 070	0.039	–	–
Penta-1,2,3,4-tetraene	TD-B3LYP	50 100	2.046	49 630	2.067	–	–
		62 620	0.012	58 670	0.014	–	–
	SAC-CI	55 630	2.330	55 040	2.388	–	–
		70 390	0.015	64 180	0.015	–	–
Hydrogen cyanide	TD-B3LYP	65 990	0.019	65 580	0.015	65 360	0.013
		72 620	0.001	72 060	0.001	70 870	0.001
	SAC-CI	77 730	0.018	75 500	0.027	–	–
		93 800	0.010	92 350	0.004	–	–
Dicyan	TD-B3LYP	56 180	0.029	56 150	0.026	–	–
		71 780	1.389	71 104	1.573	–	–
	SAC-CI	68 540	0.052	68 720	0.050	–	–
		90 720	1.539	90 800	1.789	–	–

three functionals used. Calculated positions of the first strong band with ethene amount to 48 900 cm^{-1} (B3LYP, TZ) and 50 103 cm^{-1} (PBE1PBE, TZ), which agree well with the observed value[21]. However, agreements and disagreements of this sort are of limited value and preclude making a generalization. In the present situation it is still highly desirable to treat extensive sets of data for structurally related species.

Polyynes

Our calculations (TD-B3LYP, aug-cc-pVTZ) have been performed for ethyne through tetradecaheptayne and also for cumulenes having a total of three to nine carbon atoms. Electronic spectral data of varying quality are available in literature for polyynes[18] and derivatives[19] thereof. Structural formu-
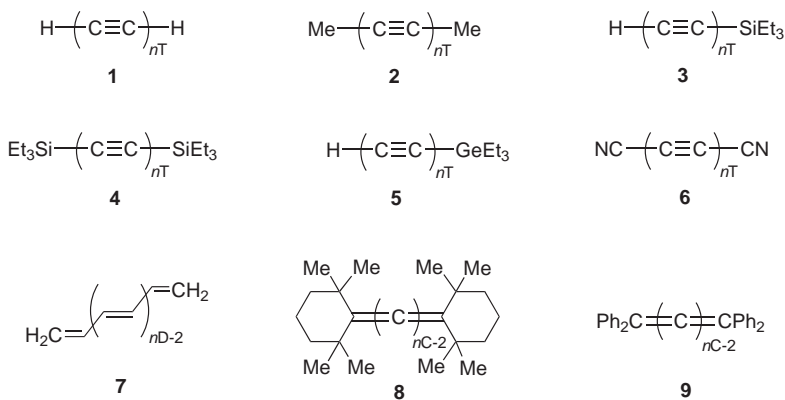
TABLE II
The first two electronic transitions calculated by various versions of the TD DFT method for cc-pVDZ and cc-pVTZ basis sets. For comparison also SAC-CI data are presented

Species	B3LYP		HCTH		PBE1PBE		SAC-CI	
	$\tilde{\nu}$	f	$\tilde{\nu}$	f	$\tilde{\nu}$	f	$\tilde{\nu}$	f
DZ basis set								
Ethene	49 340	0.255	62 830	0.283	50 740	0.272	70 770	0.457
	59 860	0.019	66 030	0.017	62 530	0.020	73 570	0.025
Dicyan	56 180	0.029	52 250	0.020	57 100	0.029	68 540	0.052
	71 780	1.389	70 200	1.269	72 570	1.437	90 720	1.539
Ethyne	72 200	0.006	71 060	0.007	75 380	0.007	85 730	0.007
	79 580	0.739	80 280	0.683	80 090	0.762	98 940	1.215
TZ basis set								
Ethene	48 910	0.268	58 690	0.302	50 100	0.280	67 920	0.445
	57 010	0.030	56 960	0.016	59 330	0.031	69 260	0.034
Dicyan	56 150	0.026	52 160	0.019	57 020	0.026	68 720	0.050
	71 100	1.573	69 680	1.400	71 770	1.562	90 800	1.789
Ethyne	69 160	0.014	66 820	0.014	71 870	0.015	81 750	0.017
	77 040	0.779	76 720	0.707	77 560	0.791	93 570	1.115

las of the systems under study are depicted in Scheme 1. A sophisticated gas-phase and the usual solution data for polyynes **1** (Scheme 1; nT up to 5) are available[18a,18b] (Table III). Moreover, the first intensive bands for long polyynes (nT up to 12, except 11) were recorded[18c]. As to the ethyne derivatives, positions of some absorption maxima for 1,ω-dimethyl- (**2**), 1-(triethylsilyl)- (**3**) and 1,ω-bis(triethylsilyl)- (**4**), 1-(triethylgermyl)- (**5**), and 1,ω-dicyanopolyynes (**6**) were published[19]. The longest-wavelength bands of polyynes, corresponding to two forbidden transitions, $^1\Sigma_g^+ \to {}^1\Sigma_u^-$ and $^1\Sigma_g^+ \to {}^1\Delta_u$, is of medium intensity (log ε amounts to 2.5–3) and is denoted A by Kloster-Jensen[18b]. The next band marked B is very intensive (log ε > 5) and was ascribed to the $^1\Sigma_g^+ \to {}^1\Pi_u$ transition. The next band, C, is located between the A and B bands only in the case of ethyne.

The electronic spectrum of the first member of the series, ethyne, is a rather difficult task, which is evident from a recent, highly sophisticated study by Lischka and co-workers[20]. In this connection the position of the first experimentally observed bands is topical: 42 200–47 600 cm^{-1} ($^1\Sigma_u^-$) and 48 300–64 500 cm^{-1} ($^1\Delta_u$) (ref.[21]), 52 900 cm^{-1} (ref.[18b]), and the latest data at 57 300 cm^{-1} ($^1\Sigma_u^-$) and 58 100 cm^{-1} ($^1\Delta_u$) by Dressler and Allen[22]. The first allowed degenerate transition, calculated in this work, is at 58 760 cm^{-1} (TD DFT with augmented TZ basis set).

Dimethyl substitution of ethyne is related to a significant bathochromic shift of both longest-wavelength bands (weaker and stronger) by about 1.5 eV (TD-B3LYP and SAC-CI with TZ); the observed shift amounts to

SCHEME 1

Attention: While nT stands for the number of the CC triple bonds in polyynes, nC means the total number of conjugated C atoms in the cumulene chain (terminal C atoms are also counted)

TABLE III
Observed absorption maxima ($\tilde{\nu}$ in cm^{-1}) of polyynes H(C≡C)$_{nT}$H and disubstituted derivatives thereof (dimethylpolyynes (diMe), bis(triethylsilyl)polyynes (diSiEt$_3$), and dicyanopolyynes (diCN)). Data in the gas phase (g) and in solution (sol)

nT	A (g)[a]		B (g)[a]		C (g)[a]		A (sol)[a]	B (sol)[a]	B (sol)[d,e]		diMe[f] A (sol)		diMe[f] B (sol)		diSiEt$_3$[g,h] B (sol)	diCN[i] B (sol)
	$10^{-3}\tilde{\nu}$	$10^{-3}\tilde{\nu}$[b]	$10^{-3}\tilde{\nu}$	$10^{-3}\tilde{\nu}$[b]	$10^{-3}\tilde{\nu}$	$10^{-3}\tilde{\nu}$[b]	$10^{-3}\tilde{\nu}$[c]	$10^{-3}\tilde{\nu}$	$10^{-3}\tilde{\nu}$	log ε	$10^{-3}\tilde{\nu}$	log ε	$10^{-3}\tilde{\nu}$	log ε	$10^{-3}\tilde{\nu}$	$10^{-3}\tilde{\nu}$
1	52.8	59.1	74.6	74.8	65.8	66.0	–	–	–	–	–	–	–	–	–	–
2	41.5	43.2	63.5	60.8	69.4	69.2	42.4; 44.6	–	–	–	41.7	2.60	–	–	–	–
3	34.0	36.3	54.8	54.6	69.8?	–	34.3; 36.2	–	–	–	37.2	2.30	>48	5.18	–	–
4	29.8	–	48.7	48.2	–	–	30.9; 33.0	44.3	44.3	5.25	32.5	2.30	42.5	5.44	39.1	–
5	26.7	–	44.0	–	–	–	27.9; 29.9	39.8	39.9	int.	28.5	2.40	37.8	5.64	35.9	43.1
6	–	–	–	–	–	–	–	–	36.6	5.47	26.2	2.30	34.7	5.70	33.5	38.6
7	–	–	–	–	–	–	–	–	33.9	int.	–	–	–	–	31.5	33.5

[a] Maxima of the A, B, and C bands taken from Fig. 6 of ref.[18b]. In the case of solution data for the A band positions of two vibrational peaks are presented because they are of similar intensity. [b] Most intense vibrational peaks of the A, B, and C bands on the basis of Tables I–III and Figs 1 and 2 of ref.[18b]. [c] Two most intensive vibrational bands. [d] Taken from ref.[18c]. [e] Moreover, absorption maxima (in cm^{-1}) for longer polyynes are available in ref.[18c]: hexadecaoctayne 31 700, log ε = 5.48; octadecanonayne 30 200, very intensive band; icosadecayne 28 700, very intensive band; doicosaundecayne 26 700, very intensive band. [f] Taken from ref.[19a]. [g] Taken from ref.[19a]. [h] Absorption maxima (in cm^{-1}) of longer derivatives: hexadecaoctayne 29 900, octadecanonayne 28 700, icosadecayne 27 400, doicosaundecayne 25 800; ref.[19c]. [i] Taken from ref.[19a]; absorption maxima (in cm^{-1}) of longer derivatives (total number of triple bonds are included): 33 000 (**8**); 31 100 (**9**); 29 500 (**10**).

about one half of the calculated value. The nature of transitions remains unchanged with respect to the parent compound. In contrast mono-methylation leads to an even larger bathochromic shift (TD-B3LYP/TZ: 44 930 and 63 020 cm^{-1}); however, both are only very weakly allowed.

Calculated absorption curves (TD-B3LYP, aug-cc-pVTZ) for polyynes **1** (nT = 2–7) are presented in Fig. 1. Positions of maxima of experimental absorption bands are indicated in those figures exactly, while intensities are visualized semiquantitatively only: shorter and longer lines mean medium- and high-intensity absorption. The point is that with the gas-phase data[18a,18b] only relative absorption intensities are available; moreover, with quite a few solution data[18c] sufficiently accurate concentrations are not known and in these instances also only relative intensities are available. This is the main reason for our atypical way of making comparison between calculated and observed data (Table III), specifically for inserting the observed absorption positions into calculated absorption curves. The overall agreement between calculated and observed band positions is reasonably good.

Derivatives of Polyynes: Extrapolation to Infinity

In order to get an overall feeling of the situation in the whole realm of polyynes and derivatives thereof, the wavenumbers of the first intensive absorption bands (B band) are plotted against the reciprocal values of the number of triple bond, $1/n$T (Fig. 2). The positive feature of such plots, in contrast to the Lewis–Calvin[23] plot, λ^2 vs n, where λ stands for the wavelength of the absorption maximum, is that one that passes from a rather difficult extrapolation to infinity to an easier extrapolation to zero. Regarding a really linear dependence it would be easy to estimate the positions of the B bands for infinite systems on the basis of simple linear extrapolations. However, it is obvious from Fig. 2 that the dependences are not strictly linear. On closer examination, it becomes clear that significant deviations from linearity are associated with shorter polyynes which are not included in Fig. 2. For this reason the estimates of the B band positions for the infinite chain are based on data for higher polyynes beginning with dodecahexayne, which deviate significantly less from linearity.

The data are split into two classes, namely, molecules (polyynes and their simple derivatives, $^1\Sigma^+$), and anions resulting from the split of a proton ($^1\Sigma^+$ ground state) as well as radical anions and their monocyano derivatives ($^2\Pi$ ground state). The extrapolated values (with a parabolic function) for infinite chains suggest that the first band of polyynes and classical deriva-
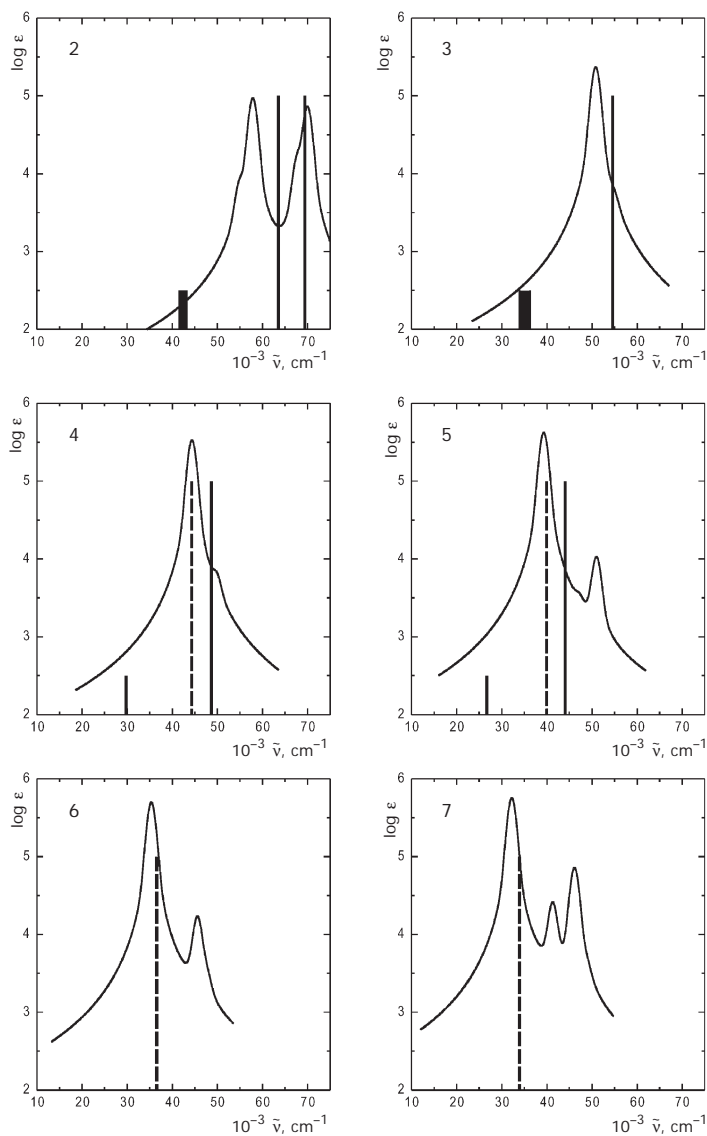
FIG. 1

Electronic spectral data for a series of polyynes **1**. The number of C≡C triple bonds is indicated in the left corner of the individual figures. The curves are calculated and the experimentally observed positions ($10^{-3} \tilde{\nu}$ in cm^{-1}) of absorption maxima are visualized by continuous and dashed lines; they correspond to gas-phase[18a] and solution data[18a,18b], respectively. Short and long lines indicate medium and strong absorption bands

tives thereof might by located at about 15 000 to 19 000 cm^{-1}. The very small if not vanishing value for infinite polyyne anions and radical anions is understandable because of significant suppression of bond alternation. This was reported recently in a study of ground state properties of polyynes[25].

We are not sure whether the recorded intensive band of anions derived from polyynes ($^1\Sigma^+$) corresponds to the B bands of the parent compounds. We specifically considered the shift larger than expected on the basis of experience. However, our spectral calculations (TD-B3LYP, DZ) for H–C≡C$^-$ and H–C≡C–C≡C$^-$ lead to shifts of about 10 000 cm^{-1} which fit very well with the experimentally observed shift. Let us add that in the case of the ethyne anion, the intensive first band is preceded by a very weak n→π* band. However, already with the butadiyne anion, the n→π* band is only the second and obviously buried by the B band.

While dimethyl substitution exerts a hypsochromic effect on the A band, the opposite is true with the B band. An analogous shift is observed with the B band of disilyl derivatives but the effect is, in this case, more pronounced. Obviously, in the case of dicyano derivatives, isoelectronic species have to be compared, i.e., ethyne and hydrogen cyanide, butadiyne and dicyan, etc. (vide supra). Evidently, passing to 1,ω-dicyanopolyynes
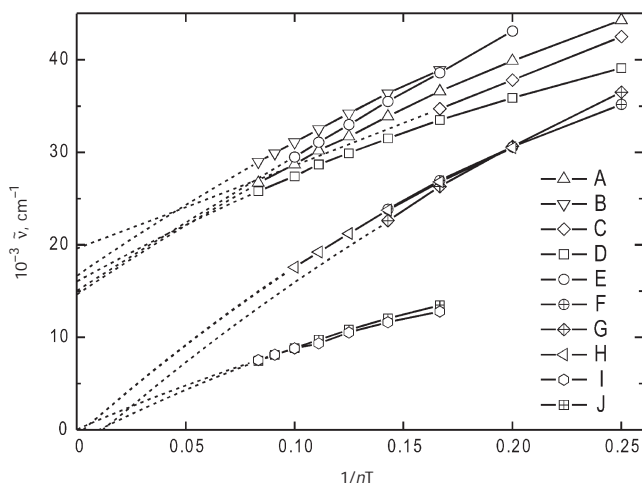

FIG. 2

Wavenumbers $\tilde{\nu}$ of the first intensive bands (B bands[18a] in the case of polyynes) plotted against $1/n$T. Designation: A, polyynes; B, polyynes[9a]; C, dimethylpolyynes; D, bis(triethylsilyl) derivatives; E, dicyano derivatives; F, closed-shell anions[9d]: $C_{2n}H^-$, G, $C_{2n-1}N^-$ and H, $C_{2n}H^-$ in gas phase; radical anions[9a]: I, $HC_{2n}H^{\bullet-}$ and J, $HC_{2n-1}N^{\bullet-}$

brings about a significant bathochromic shift (band B). Calculated shifts (TD-B3LYP, TZ) agree with the observed ones.

Cumulenes

Lack of stability of cumulenes is responsible for the fact that allene (propadiene) is the only representative of the D_{2d} series that was isolated. Alkyl, cycloalkyl, phenyl, and halo derivatives (D_{2h} series) in which no hydrogen atom remains unsubstituted were prepared and studied[26]. For analysis of spectral features, derivatives **8**, Scheme 1, 1,ω-(bis(2,2,6,6-tetramethylcyclo-hexylidene) polycumulene) are the most appropriate. They are, as far as the electronic structure is concerned, closely related to tetra-*tert*-butyl derivatives.

We will deal now with cumulenes more specifically (Table IV). The first point which has to be made is a split of data for cumulenes into two classes, classes with the D_{2h} and D_{2d} symmetry. This was observed with various ground-state properties[11] and it is clearly seen in Fig. 3a where calculated wavenumbers of the longest-wavelength intensive band of cumulenes (D_{2h}, D_{2d}) are plotted against nC. This split and analysis of electronic spectra were discussed semiempirically in a valuable study initiated years ago[24]. In Fig. 3b a similar dependence is demonstrated for the experimentally observed first and second band maxima.

Figure 4 illustrates how calculated absorption curves for methane and allene are combined with experimentally observed spectral features[21].

TABLE IV
Observed absorption maxima[12] ($\tilde{\nu}$ in cm^{-1}) of substituted cumulenes **8** and **9**

	8				**9**					
nC	I[a]		II		I		?		II	
	$10^{-3}\,\tilde{\nu}$	log ε	$10^{-3}\,\tilde{\nu}$	log ε	$10^{-3}\,\tilde{\nu}$	log ε	$10^{-3}\,\tilde{\nu}$	log ε	$10^{-3}\,\tilde{\nu}$	log ε
4	37.0	4.48	51.0[b]	5.0	24.4	4.60	32.5	3.76	37.5	4.52
6	29.7	4.52	42.0	5.24	20.6	4.84	27.6	4.16	36.7	4.61
									40.0	4.67
8	25.0	4.20	35.3	5.34	19.0	4.80	22.4	4.52	32.7	4.92
10	21.5	4.17	31.0	5.40	16.6	4.70	19.0	4.64	27.6	5.10

[a] nC = 2, i.e. tetramethylethene, $10^{-3}\,\tilde{\nu}$ = 52.2 cm^{-1}. [b] Estimates based on extrapolation.
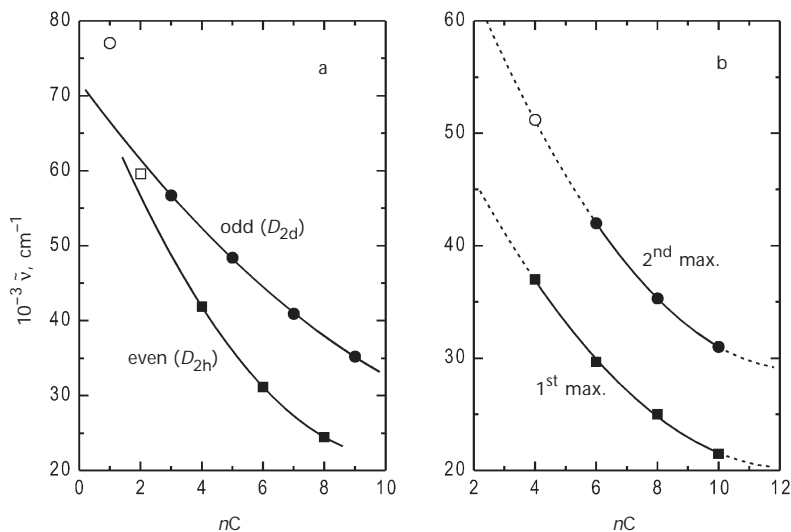
FIG. 3

a Calculated wavenumbers of the first intensive absorption bands for cumulenes having odd (D_{2d}) or even (D_{2h}) number of carbon atoms plotted against the total number of carbon atoms, nC; b Experimental wavenumbers of the first and the second intensive bands[25a] of substituted even (D_{2h}) cumulenes, **8**, plotted against the total number of carbon atoms, nC. Empty symbols in a stand for methane (○) and ethene (□). Empty symbol (○) in b concerns the extrapolated value for the C4 cumulene. Parabolic fits are used throughout
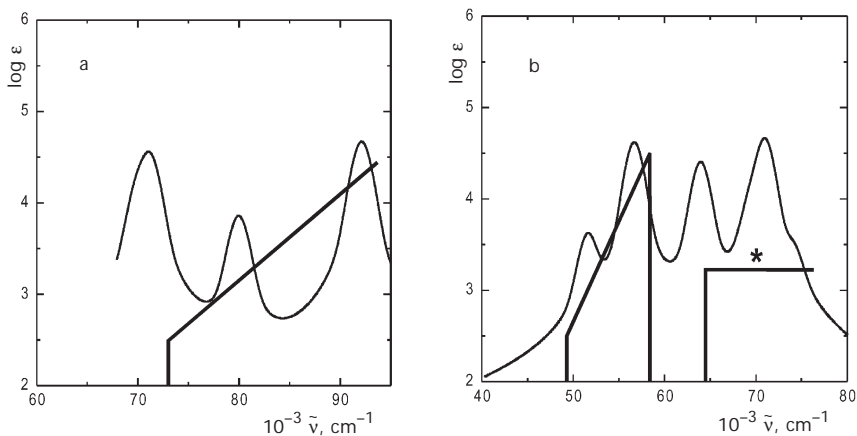
FIG. 4

Electronic spectral data for cumulenes with odd number of carbon atoms ($10^{-3}\ \tilde{\nu}$ in cm^{-1}); methane is a purely formal member of this series. Calculated absorption curves; experimentally observed features of methane (a) and allene[21] (b) are semiquantitatively indicated by continuous lines. In the region labeled by *, several intensive bands were observed

Clearly, methane is only purely formal cumulene with a single carbon atom. Additional details are presented in the caption to Fig. 4. On the whole, qualitatively speaking, there is correspondence between calculated and observed characteristics.

Figure 5 concerns cumulenes with even number of carbon atoms. Again, ethene is a part of this series only formally. It can be said that the position of observed one or two absorption bands of tetraalkyl substituted derivatives is essentially reproduced by calculations for the parent (unsubstituted
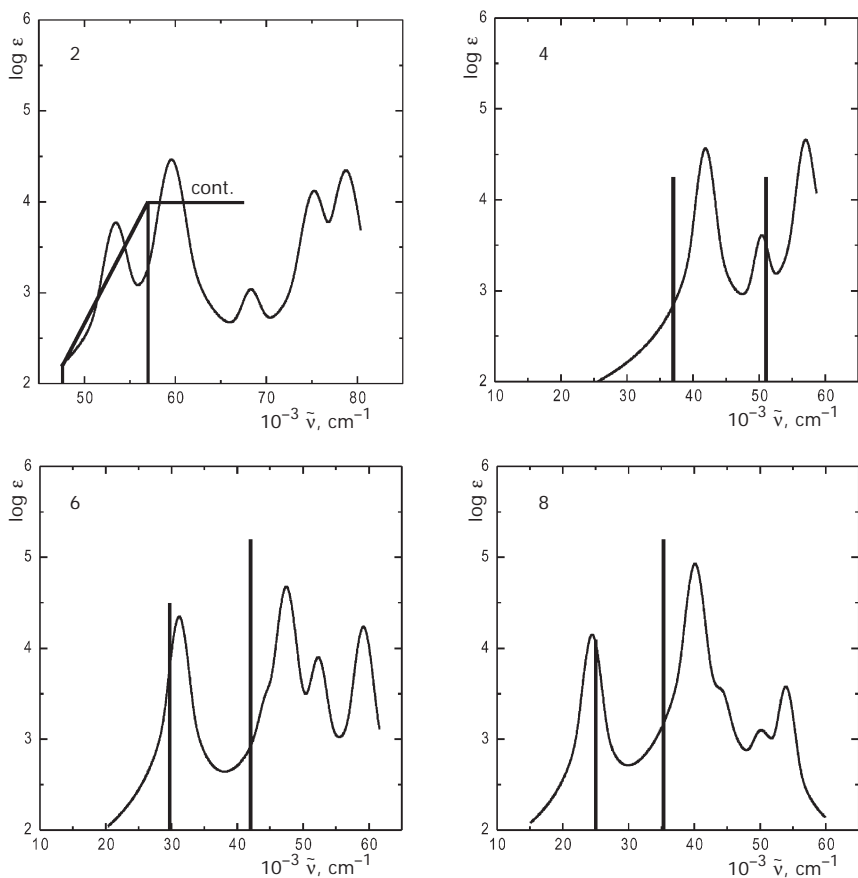
F_{IG.} 5

Electronic spectral data for cumulenes[26a] **8** with even number of carbon atoms; this number of carbon atoms (*n*C) is indicated in the left corner of the individual figures. The curves are calculated and the experimentally observed position ($10^{-3}\ \tilde{v}$ in cm^{-1}) of absorption maxima (for tetrasubstituted derivatives **8**) is visualized by continuous lines. Ethene[21] is only a formal member of the cumulene series

systems). Regarding ethene, experimental features are associated with the unsubstituted hydrocarbon[21]. No doubt, if the influence of the tetraalkyl substitution would be properly taken into consideration, the calculated positions of the absorption maximum would shift by about 4000–8000 cm^{-1} bathochromically, which is almost exactly the value between positions of calculated and observed maxima in Fig. 5 (cf. the influence of alkyl substitution in refs[27e,27f]).

In Fig. 6 a comparison is made of calculated spectral features of C4 and C6 cumulenes and experimental absorption curves for substituted cumulenes[8]. Details are given in the caption to Fig. 6.

Derivatives of Polyenes: Extrapolation to Infinity

Recently, several studies dealt with quantum-chemical interpretation of electronic spectra of polyenes[27a–27c]. It was shown that TD DFT works satisfactorily with these systems[27a]. It is of the essence to treat seven available sets of data for polyene-like systems[27d–27f] along the same lines as done in Fig. 2 for polyynes and related systems. The situation with these two ensembles is analogous: real polyenes **7**, i.e., systems with pronounced bond
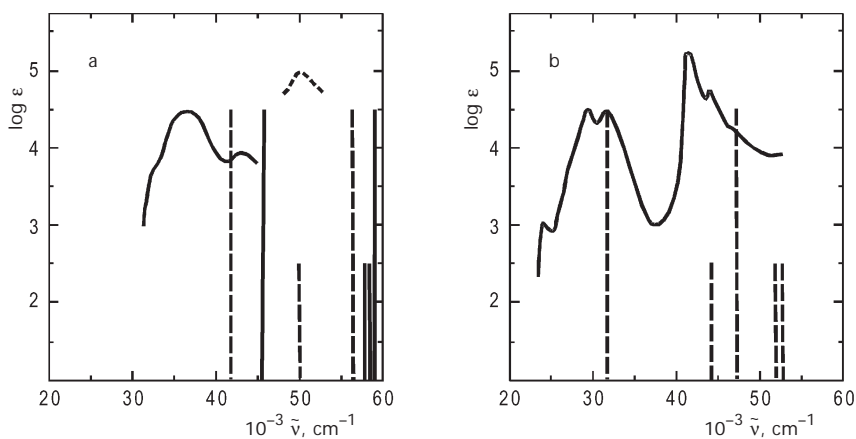

F𝐈𝐆. 6

Experimental absorption curves[24,26a] of substituted cumulenes **8**: a $nC = 4$; b $nC = 6$. The second absorption band in a, represented by a dotted line, was obtained by extrapolation from spectral data[26a] presented in Fig. 3. Intensities of the calculated transitions are indicated by long and short lines for very strong and medium intensive bands, respectively. Theoretical data are indicated by dashed lines for TD DFT and continuous lines for MS-CASPT2(6,10)/ANO-S(4s3p2d(3s2p)+Rydberg(1s1p1d) methods

alternation tend to the limiting value of the position of the longest-wavelength band (Fig. 7). This value amounts approximately to $14\,000$ cm^{-1}. Again, at first, superficial sight, some of the dependences could be approximated by straight lines. Some, however, are obviously curved: this pertains primarily to merocyanines and cations of odd polyenes (i.e., derivatives of the allyl cation). On closer inspection all the dependences deviate, at least slightly, from linearity. Fitting all the points for a selected class of compounds can be easily insetted by means of quadratic parabolic curves. Extreme instances are represented by all-*trans* polyenes and 1,ω-dimethyl derivatives thereof, i.e., systems with pronounced bond alternation and by ions of even or odd polyenes with bonds tending to uniformity. The same feature is associated with systems exerting, classically speaking, symmetrical resonance structures, i.e., symmetrical cyanines (*1*), oxonoles (*2*), and the allyl cations substituted by a polyenic chain (*3*).

$$(1)$$

$$(2)$$

$$(3)$$
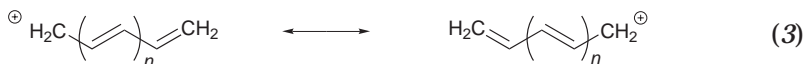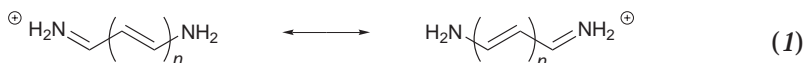
In contrast, the role of ionic structure with classical polyenes (*4*) is small and probably the same holds true, except first members, for the merocyanine series (*5*).

$$(4)$$

$$(5)$$
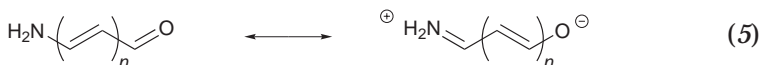
The plot in Fig. 7 suggests that the ionic form (*5*) in merocyanines contributes significantly only in the lower members of the series while in higher members a real polyenic character predominates.

CONCLUSIONS

During the last few years polyynes and cumulenes have become intensively studied systems[11]. They were considered rigid rods. Experimental and theoretical evidence showed clearly that they possess, with increasing chain length, very soft deformation vibrations. Therefore, they are flexible rather than rigid rods. This study has shown that a version of TD DFT theory enabled reproduction of the electronic spectra of these systems. Specifically, this procedure with B3LYP functional and with augmented TZ basis set represents a good compromise between accuracy and economy, reproducing correctly positions and intensities of the two longest-wavelength bands.

The situation with small systems (containing up to three or four first-row atoms and a few hydrogen atoms) is more difficult. Experimentally, measurements in a less accessible region, vacuum UV, are necessary and the theoretical interpretation is more difficult because of the significant role of
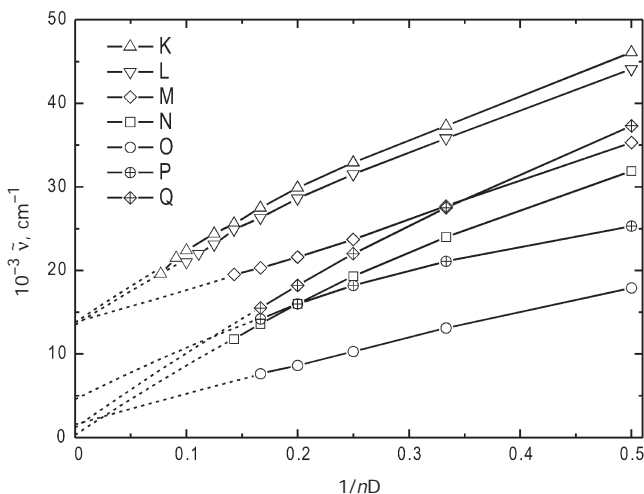

FIG. 7
Wavenumbers $\tilde{v}$ of the first intensive bands[27d–27f] plotted against $1/n$D. Designation: K, polyenes; L, 1,ω-dimethylpolyenes; M, merocyanines; Q, symmetric cyanines; N, oxonols; P, cations of odd polyenes; O, radical anions of polyenes, calculated values[27g]

Rydberg transitions. Therefore, when continuing this study, a careful comparison of several computational schemes would be advisable. Moreover, these systems will require rather extensive individual care.

It is not yet possible to make a definite decision about the nature of infinite polyynes, cumulenes, polyenes and derivatives thereof. The situation is clear with systems possessing clear bond alternation. Such systems would absorb in the region between 14 000 and 17 000 cm^{-1}. The belief that systems like polyenic alkyl cations or symmetrical cyanines would act as conductors, probably cannot be proved at the moment, being neither experimental nor theoretical. But the more it continues to be a captivating problem.

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