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Semi-empirical Parameters for the π-Electron System in the Carbon-Carbon Triple Bond

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A modification of the Pariser-Parr-Pople approximation has been extended to include parameters appropriate to the carbon-carbon triple bond. Mobile bond orders, ionization potentials, and electronic transition energies have been calculated and compared with available experimental results.

Numerous semi-empirical calculations on π-electron systems have been performed in the past years. However, only in relatively few cases the calculation schemes have been designed to treat triple bonds. This is the first of two articles on the inclusion of the carbon-carbon triple bond and the cyanide group in a semi-empirical calculation method.

Roos and Skancke [1,2] developed a new scheme for the evaluation of semi-empirical parameters in the Pariser-Parr-Pople (PPP) approximation,[3–5] and applied it to a number of conjugated hydrocarbons. In the present paper the parameter scheme is extended to include parameters appropriate to the carbon-carbon triple bond, and calculations are performed for a set of acetylene derivatives.

METHOD OF CALCULATION

The general method as outlined before [1] is here modified by the inclusion in the atomic orbital basis of two p orbitals from each triple-bonded atom, whereby the total basis is divided into two mutually orthogonal subsets. The PPP approximation in this case involves the following assumptions concerning integrals over basis orbitals:

$$S_{\mu\nu} = (\mu|\nu) = \delta_{\mu\nu} \tag{1}$$

$$\alpha_\mu = (\mu|H^{\text{core}}|\mu) \neq 0 \tag{2}$$

$$\beta_{\mu\nu} = (\mu|\mathrm{H}^{\text{core}}|\nu) \neq 0 \quad \mu \text{ and } \nu \text{ on neighbouring atoms and belonging to the same subset} \tag{3}$$

$$(\mu|H^{\text{core}}|\nu) = 0 \qquad \text{in all other cases} \tag{4}$$

$$\gamma_{\mu\nu} = (\mu\mu|\nu\nu) \neq 0 \tag{5}$$

$$K_{\mu\nu} = (\mu\nu|\mu\nu) \begin{cases} \neq 0 \text{ method A} \\ = 0 \text{ method B} \end{cases} \mu \text{ and } \nu \text{ on the same atom} \tag{6}$$

$$(\mu\sigma|\nu\lambda) = 0 \qquad \text{in all other cases} \tag{7}$$

It is to be noticed that (1) and (4) are exactly valid when the orbitals μ and ν belong to different subsets.

The core integral α_μ may according to Goeppert-Mayer and Sklar [6] be rewritten in the following way

$$\alpha_\mu = W_\mu - (n_\mu - 1)\ \gamma_{\mu\mu} - \sum_{\nu \neq \mu} n_\nu\ \gamma_{\mu\nu} \tag{8}$$

where n_μ is the neutral charge of the orbital μ.

The special assumptions introduced by Roos and Skancke [1] can now be summarized as follows: The atomic parameter W_μ is assumed dependent on the surroundings to the atom by the relation

$$W_\mu = W_\mu{}^\circ + \sum_\nu \Delta W_\mu(\nu) \tag{9}$$

where $\Delta W_\mu(\nu)$ means a change due to the neighbouring atom ν and varying with the bond distance $R_{\mu\nu}$ according to

$$\Delta W_\mu(\nu) = \Delta W_\mu{}^\circ(\nu) + \delta_{\mu\nu}{}^W(R_{\mu\nu} - R_{\mu\nu}{}^\circ) \tag{10}$$

Here $R_{\mu\nu}{}^\circ$ is a reference distance chosen for each type of bond involved. Furthermore, for a pair of bonded atoms, the integrals $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$ are also assumed dependent on the bond distance by linear relations:

$$\beta_{\mu\nu} = \beta_{\mu\nu}{}^\circ + \delta_{\mu\nu}{}^\beta(R_{\mu\nu} - R_{\mu\nu}{}^\circ) \tag{11}$$

$$\gamma_{\mu\nu} = \gamma_{\mu\nu}{}^\circ + \delta_{\mu\nu}{}^\gamma\ (R_{\mu\nu} - R_{\mu\nu}{}^\circ) \tag{12}$$

For all actual types of atoms and bonds the quantities $W_\mu{}^\circ$, $\Delta W_\mu{}^\circ(\nu)$, $\delta_{\mu\nu}{}^W$, $\beta_{\mu\nu}{}^\circ$, $\delta_{\mu\nu}{}^\beta$, $\gamma_{\mu\nu}{}^\circ$, and $\delta_{\mu\nu}{}^\gamma$ are treated as semi-empirical parameters to be determined from experimental information.

The question whether the one-center exchange integral $K_{\mu\nu}$ should be neglected in the present extension of the zero differential overlap (ZDO) assumption, needs some comments. Pople *et al.*[7] analyzed corresponding problems in the simplified SCF theory for all valence electrons of a molecule. They found two calculation schemes that were invariant under simple transformations among the atomic orbitals on a given atom. These are the CNDO (complete neglect of differential overlap) and NDDO (neglect of diatomic differential overlap) schemes, of which only the more approximate CNDO neglects one-center exchange integrals.

The ZDO assumption of π-electron theory corresponds closely to NDDO, and the desired transformation invariance is thus only preserved when the one-center $K_{\mu\nu}$ is retained. On the other hand, in the π-electron calculations for planar or linear molecules there is one preferred choice of the basis. A lack

of transformation invariance will accordingly not lead to ambiguities in this special case.

In the present work two different sets of semi-empirical parameters have been developed and used. The first (called set A) retains the one-center $K_{\mu\nu}$, the second (called set B) is simplified further by neglecting all $K_{\mu\nu}$ without doing any other change in the formalism. The remaining parameters have been determined for each of the two methods separately. It is a point of some interest, to what degree the parameter determination in B compensates the effects of neglecting the exchange integral.

DETERMINATION OF SEMI-EMPIRICAL PARAMETERS

For sp^2 hybridized carbon atoms and bonds between them, the parameters were taken directly from Roos and Skancke.[1,2] For acetylene and the linear polyacetylene chains with only *sp* hybridized carbon atoms, the appropriate parameters have been determined from experimental information. Parameters for bonds involving one *sp* and one sp^2 hybridized atom, finally, have been fixed by some simple interpolation rules.

Within the group of molecules treated here, an *sp* hybridized carbon atom may take part in three types of carbon-carbon bonds, an *sp-sp* triple bond, an *sp-sp* single bond, or an *sp-sp*^{2} single bond. As the triple bond is invariably present, the acetylene value of the parameter W_C is adopted as the general term W_C° (eqn. (9)) for *sp* hybridized carbon. If the atom is also involved in one type of C–C single bond, a correction term ΔW_{C1} (C_2) is needed, meaning a correction to the parameter W for an *orbital* on C_1, due to the *atom* C_2. The relation

$$W_{C1}(C_2) = W_{C2}(C_1) \tag{13}$$

which is obviously valid when both atoms have the same hybridization, is here assumed to hold even in the case of one *sp* and one sp^2 hybridized atom. Furthermore, in this latter case no distinction is made between the correction terms to the two different orbitals on C_1. In this way the number of parameters is reduced.

The variations in bond length within each of the three bond types described have been neglected, an assumption supported by available experimental material. The second term in eqn. (10) therefore vanishes for these bonds, and the parameter $\delta_{\mu\nu}{}^W$ is not needed.

The one-center two-electron integrals $\gamma_{\pi\pi}$, $\gamma_{\pi\bar{\pi}}$ and $K_{\pi\bar{\pi}}$ were given values obtained from atomic spectral data [8] and are listed in Table 1. In version B of the calculations, $K_{\pi\bar{\pi}}$ as discussed was put equal to zero, and the two others kept unchanged.

In order to limit the number of independent semi-empirical parameters further, the parameters γ_{CC}, β_{CC}, and ΔW_C(C) for the *sp-sp*^{2} single bond were simply put equal to the arithmetic mean of the corresponding butadiene and diacetylene parameters. The observed lengths of the long bond in butadiene, vinyl acetylene, and diacetylene are 1.467 Å, 1.425 Å, and 1.376 Å, respectively,[9–11] making this assumption quite reasonable as bond-length effects and hybridization effects on the parameters are concerned.

For nearest neighbours the integral $\gamma_{c\bar{c}}$ over orthogonal orbitals was related to the corresponding γ_{cc} (parallel orbitals) by assuming

$$(\gamma_{c\bar{c}}/\gamma_{cc})_{semiemp.} = (\gamma_{c\bar{c}}/\gamma_{cc})_{teor.} \quad (14)$$

On the basis of Slater orbitals with the effective charge of Duncanson and Coulson,[12] the right hand side of (14) was found equal to 0.962, 0.971, and 0.973 for the actual bond distances 1.205 Å, 1.376 Å, and 1.425 Å.

Repulsion integrals $\gamma_{\mu\nu}$ for non-neighbours were calculated by the uniformly charged sphere approximation [13] using a sphere diameter of 1.47 Å. When the two orbitals involved had perpendicular axes, a generalized version [14] of the approximation was used.

In this way only six independent parameters remained to be determined from experimental data: β_{cc}°, δ_{cc}^{β}, γ_{cc}°, δ_{cc}^{γ}, W_c°, and $\Delta W_c(C)$, all C's standing for *sp* hybridized carbon. The ionization potential (IP) of acetylene (I)[15] and the two lowest IP's of diacetylene (II)[16] were used for this purpose, together with the lowest ${}^1\Sigma_g^+ - {}^1\Sigma_u^+$ transition for each of the molecules acetylene,[22] triacetylene (III),[23] and tetraacetylene (IV).[23] The lowest singlet-singlet transition for divinyl acetylene (VIII),[24] and the two lowest for phenyl acetylene (IX)[25,26] were also taken into account. Thus six independent parameters were fixed by the use of nine observed values. These were all satisfactorily reproduced, as is seen in Tables 3 and 5 where experimental data used for parameter determination are labelled by an asterisk.

All the parameter values used in the present work are listed in Table 1.

Table 1. Semi-empirical parameters for sp^2 and *sp* hybridized carbon atoms.

Parameter	Roos and Skancke [1,2]	This work, method A		This work, method B	
	sp^2 hybridized carbon atoms	*sp* hybr. carbon at.	sp-sp^2 C–C bond	*sp* hybr. carbon at.	sp-sp^2 C–C bond
R_{cc}°	1.397 Å	1.205 Å	1.425 Å	1.205 Å	1.425 Å
$\gamma_{\pi\pi}$	11.97 eV	11.97 eV		11.97 eV	
$\gamma_{\pi\bar{\pi}}$		10.68 eV		10.68 eV	
$K_{\pi\bar{\pi}}$		0.645 eV		0	
γ_{cc}°	6.91 eV	9.00 eV	7.74 eV	9.29 eV	7.74 eV
δ_{cc}^{γ}	−3.99 eV/Å	−0.91 eV/Å		−2.59 eV/Å	
β_{cc}°	−2.42 eV	−3.15 eV	−2.09 eV	−3.20 eV	−2.09 eV
δ_{cc}^{β}	3.05 eV/Å	6.92 eV/Å		7.16 eV/Å	
W_c°	−9.84 eV	−9.42 eV		−9.56 eV	
$\Delta W_c(C)$		0,46 eV	0.59 eV	0.45 eV	0.59 eV
$\Delta W_c^{\circ}(C)$	0.07 eV				
δ_{cc}^{W}	9.22 eV/Å				

EXPERIMENTAL INFORMATION ON THE ELECTRONIC SPECTRA OF ACETYLENE AND THE POLYACETYLENES

In this section the possibility of estimating vertical π-π^* transition energies from available experimental data will be examined.

1. Acetylene. The absorption spectrum of acetylene in the vacuum UV has been thoroughly investigated by several authors.[17–22] It is dominated by strong Rydberg bands extending from 8.0 eV (1550 Å) to the ionization limit at 11.4 eV. Non-Rydberg absorption is found in three regions, a system of very weak bands between 5 and 6.2 eV, a somewhat stronger system of overlapping diffuse bands from 6.2 to 8 eV with a maximum around 7.2 eV, and some rather strong bands in the region 9.2 – 9.7 eV, overlapping with Rydberg bands.

The first system has been analyzed in detail [18,19] and assigned to a transition to a nonlinear state ^1A_u (*trans* form) correlating with linear states $^1\sum_u^-$ or $^1\Delta_u$. The 0-0 transition occurs at 5.23 eV whereas the absorption maximum of this transition is unknown.

The diffuse band system around 7.2 eV has not been analyzed. According to Herzberg [22] it is possible but far from certain that it belongs to the transition just described.

Wilkinson [20] assigns the non-Rydberg bands around 9.5 eV to transitions to two states named B and C. The possibility cannot be definitely excluded that these bands correspond to only one transition.[27]

From the electronic configuration $(1\pi_u)^3 1\pi_g$, one $^1\sum_u^+$, one $^1\sum_u^-$, and two $^1\Delta_u$ states may be derived. The vertical transition from the ground state to the first one is allowed by the selection rules, whereas the transitions to the others are forbidden. The transition to the *trans*-bent ^1A_u state identified in the long-wave-length part of the observed spectrum and correlating with $^1\sum_u^-$ or $^1\Delta_u$, is allowed, however. The observed weakness is due to the great difference in molecular shape (Frank-Condon forbidden transition).

It seems extremely difficult to estimate the positions of the vertical transitions to $^1\sum_u^-$ and $^1\Delta_u$ states from the observed spectrum, as the absorption maxima of separate transitions below 8 eV are unknown. Furthermore, the absorption maximum in each case would be expected somewhere between the Frank-Condon forbidden 0-0 band and the symmetry forbidden vertical transition.[22]

Wilkinson [20] and Mulliken [28] suggest the B state (observed transition between 9.25 and 9.70 eV) to be identified as $^1\sum_u^+$. Earlier [17,29] the maximum at 7.2 eV had been proposed for the $^1\sum_g^+ \rightarrow {}^1\sum_u^+$ transition. The value 9.5 eV is chosen here as a reasonable rough estimate of the absorption maximum of this transition. This is in harmony with the suggestions of Wilkinson and Mulliken, and also with the alternative possibility that only one state corresponds to the B and C bands.

2. Diacetylene. The vacuum UV spectrum of this molecule [17,22] starts with a system of very weak sharp bands between 4.2 and 4.7 eV. Further there is a stronger system of diffuse bands from 4.8 eV to somewhere between 6 and 7 eV, with a maximum at about 5.2 eV. All bands found at higher energies have been classified as Rydberg bands, starting with an extremely strong absorption peak at 7.5 eV.

There are thus marked similarities with the acetylene spectrum. However, no non-Rydberg absorption corresponding to the 9.5 eV bands of acetylene, has been identified. As a conclusion, it does not seem possible from the literature available at present, to obtain any reasonable estimates of the positions of vertical π-π^* transitions from the diacetylene spectrum.

3. Tri-, tetra-, and hexaacetylene. These molecules have a very strong absorption that has been observed in methanol solutions of the di-hydroxycyclohexyl derivatives,[23] and has been classified as due to a π-π^* transition.[30] The positions of the absorption maxima and the extinction coefficients are given in Table 5. The transition energies of tri- and tetraacetylene were used for parameter determination, but because of the expected lowering of the band positions, compared with hypothetical gas phase spectra of the unsubstituted polyacetylenes, the values in parentheses in Table 5 were used to this purpose.

In addition, these molecules have a weaker absorption at longer wave length, corresponding to the diacetylene bands at 5.2 eV, and perhaps to the acetylene bands at 7.2 eV. The intensity maximum is observed at about 4.4 and 3.9 eV for tri- and tetraacetylene, and by means of a well established extrapolation procedure,[23] it is expected at 3.2 eV for hexaacetylene.

RESULTS AND DISCUSSION

The parameter values presented in Table 1 were applied in a study of the electronic structure and electronic spectra of acetylene (I) and the polyacetylenes up to hexaacetylene (II – VI), further vinyl (VII), *trans*-divinyl (VIII), and phenyl acetylene (IX). The results obtained are given in Tables 2 – 5.

The polyacetylenes were assumed to be linear and the three remaining molecules planar with bond angles of 120° and 180°. Five standard values, 1.205, 1.336, 1.376, 1.397, and 1.425 Å, were introduced for the bond lengths of triple bonds, double bonds, *sp-sp* single bonds, the bonds of the phenyl ring, and *sp-sp*^{2} single bonds, respectively. The distance-dependent parameters of all the molecules were based on these values only.

Before discussing the separate results in detail, it may be noticed that for all the ground state properties listed in Tables 2 – 4, the differences between the methods A and B are negligible.

1. Bond orders and bond distances. The calculated mobile bond orders resulting from both parameter sets are given in Table 2, together with available experimental bond distances. The carbon atoms are numbered consecutively

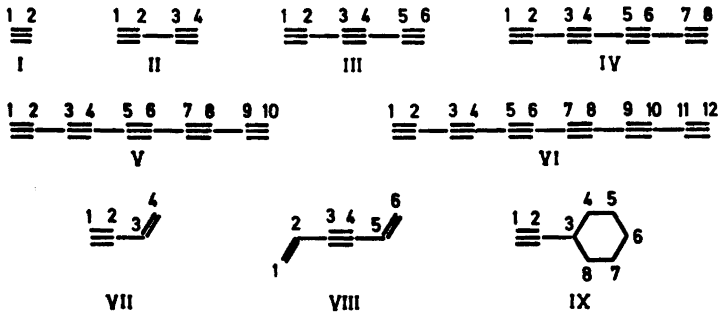

Fig. 1. Labelling of molecules and notation of atoms.

Table 2. Calculated mobile bond orders and observed bond distances (in Å). For numbering of atoms, see Fig. 1. For *sp-sp* bonds each bond order given is only the contribution from one of the π-bonds. When the second contribution is not identical, it is given separately (indicated by dashes).

Molecule	Bond	Bond orders		Obs. dist.	
		method A	method B		
I	1–2	1.000	1.000	1.205 [a]	1.212 [b] (r_g)
II	1–2	0.977	0.978	1.205 [c] (ass.)	1.218 [b] (r_g)
	2–3	0.214	0.206	1.376	
III	1–2	0.975	0.977		
	2–3	0.220	0.212		
	3–4	0.952	0.956		
IV	1–2	0.974	0.976		
	2–3	0.221	0.212		
	3–4	0.951	0.954		
	4–5	0.227	0.218		
V	1–2		0.976		
	2–3		0.212		
	3–4		0.954		
	4–5		0.218		
	5–6		0.953		
VI	1–2		0.976		
	2–3		0.212		
	3–4		0.954		
	4–5		0.218		
	5–6		0.953		
	6–7		0.219		
VII	1–2	0.966	0.967	1.207 [d]	1.209 [e]
	1′–2′	0.999	0.999		
	2–3	0.256	0.252	1.425	1.431
	3–4	0.965	0.966	1.336	1.342
VIII	1–2	0.961	0.962		
	2–3	0.269	0.265		
	3–4	0.929	0.931		
	3′–4′	1.000	1.000		
IX	1–2	0.969	0.970		
	1′–2′	0.999	0.999		
	2–3	0.244	0.240		
	3–4	0.645	0.646		
	4–5	0.670	0.670		
	5–6	0.665	0.665		

[a] Ref. 31; [b] Ref. 32; [c] Ref. 11; [d] Ref. 10; [e] Ref. 33.

Table 3. Calculated and observed ionization potentials. All values in eV. Observed values used for parameter determination are indicated by *.

Molecule	$IP_{calc.}$(A)	$IP_{calc.}$(B)	$IP_{obs.}$ PS	PI	EI
I	11.41	11.42	11.40[a]	* 11.41[b]	11.42[c]
II	10.16	10.17	* 10.17[a]		10.2[d]
	12.62	12.62	* 12.62		
III	9.54	9.56			
	11.45	11.45			
	13.05	13.05			
IV	9.19	9.20			
	10.68	10.68			
	12.17	12.17			
	13.23	13.23			
V		8.98			
		10.15			
		11.45			
		12.57			
		13.32			
VI		8.83			
		9.77			
		10.90			
		11.96			
		12.81			
		13.36			
VII	9.61	9.61			9.90[e]
	11.24	11.26			
	12.21	12.22			
VIII	8.90	8.92			
	10.55	10.54			
	11.10	11.13			
	12.59	12.61			
IX	8.82	8.81	8.77[f]	8.82[b]	9.15[g]
	9.34	9.33	9.37		
	11.20	11.22	11.21		
	11.35	11.35			
	12.79	12.79			

[a] Ref. 16; [b] Ref. 15; [c] Ref. 34; [d] Ref. 35; [e] Ref. 36; [f] Ref. 37; [g] Ref. 38.

in each molecule, starting from the triple-bond end in vinyl acetylene and phenyl acetylene (see Fig. 1).

For sp^2-sp^2 bonds a large number of bond lengths have been successfully estimated by using the relation [1]

Table 4. Calculated atomic π-electron charges. For numbering of atoms, see Fig. 1. For an *sp* hybridized atom, each charge given is only the contribution associated with one basis orbital. When the second contribution is not identical, it is given separately (indicated by dashes).

Molecule	Method	Atom								
		1′	2′	3′	1	2	3	4	5	6
I	B				1.000					
II	B				1.026	0.974				
III	B				1.034	0.967	0.999			
IV	B				1.037	0.964	1.007	0.992		
V	B				1.039	0.962	1.010	0.988	0.999	
VI	B				1.041	0.961	1.013	0.986	1.003	0.996
VII	A	1.050	0.950		1.028	0.962	0.954	1.057		
	B	1.051	0.949		1.025	0.962	0.954	1.059		
VIII	A			1.000	1.064	0.949	0.987			
	B			1.000	1.066	0.950	0.985			
IX	A	1.046	0.954		1.036	0.962	0.951	1.027	0.995	1.007
	B	1.047	0.953		1.034	0.962	0.951	1.028	0.995	1.008

$$R_{\mu\nu} = 1.517 - 0.18\, p_{\mu\nu} \tag{15}$$

where $p_{\mu\nu}$ is the mobile bond order. For *sp-sp* bonds the corresponding relation, based on some of the data [11,31] of Table 2, would roughly be:

$$R_{\mu\nu} = 1.425 - 0.11\, p_{\mu\nu} \tag{16}$$

Furthermore, a third formula with intermediate values for the constants, might be used to predict the bond lengths of *sp-sp*^{2} bonds (in acetylene derivatives as well as in the cumulenes). However, the experimental basis for the new relations indicated here is scarce, and therefore only the bond orders and no predicted distances have been listed in Table 2.

By using eqn. (16) and the bond orders of Table 2, a lengthening of 0.005 – 0.006 Å compared to acetylene, would be predicted for the terminal triple bonds of di- to hexaacetylene. The predicted lengthening of the inner triple bond is about 0.010 Å. The trend of the bond orders given suggests that these bond lengthenings will remain fairly constant for higher members of the polyacetylene series.

In a very recent electron diffraction investigation [32] that was not available when the semi-empirical parameters of the present work were determined, the r_g values 1.212 and 1.218 Å were obtained for the triple bonds of acetylene and diacetylene. The bond lengthening is in agreement with the present predictions, and in some conflict with earlier findings and assumptions,[11,31] as far as it may be regarded as significant. It is to be noticed that r_g values are not directly comparable to r_s or $r_{av.}$ values, as they, especially for triple bonds,[32] are systematically larger.

2. Ionization potentials. In Table 3 predicted molecular IP's as approximated by Koopmans' theorem are presented and compared with available

Table 5. Calculated and observed electronic spectra. Transition energies in eV. Observed values used for parameter determination are indicated by *.

Molecule	Calc. A		Calc. B		Obs.	
	ΔE	f	ΔE	f	ΔE	ε
I	5.95	forb.	5.88	forb.		
	6.08	forb.	5.99	forb.		
	6.60	forb.				
	9.50	1.21	9.49	1.21	* 9.5[a]	
II	5.06	forb.	5.07	forb.		
	5.12	forb.	5.10	forb.		
	5.58	forb.				
	6.22	forb.	6.14	forb.		
	6.42	forb.	6.33	forb.		
	6.83	forb.				
	7.27	2.22	7.28	2.20		
III	4.63	forb.	4.67	forb.		
	4.65	forb.	4.67	forb.		
	5.09	forb.				
	5.62	forb.	5.59	forb.		
	5.75	forb.	5.71	forb.		
	6.03	2.97	6.05	2.92	5.71[b](* 6.0)	119 000
IV	4.41	forb.	4.46	forb.		
	5.27	3.56	5.31	3.51	5.10[b](* 5.4)	276 000
V			4.34	forb.		
			4.83	4.03		
VI			4.27	forb.		
			4.50	4.53	4.28[b]	> 500 000
VII	5.52	forb.	5.35	forb.		
	5.55	0.20	5.51	0.17	5.56[c]	
	6.14	forb.	5.71	forb.		
	7.04	0.73	7.03	0.75		
VIII	4.90	0.58	4.90	0.54	* 4.97[d]	
	5.15	forb.	4.98	forb.		
	5.88	forb.	5.57	forb.		
	6.89	0.96	6.85	0.99	6.9	
IX	4.74	0.004	4.74	0.004	* 4.6[e]	
	5.46	0.33	5.44	0.29	* 5.3[e,f]	
	5.63	forb.	5.51	forb.		
	6.18	forb.	5.68	forb.		
	6.31	0.01	6.28	0.04		
	6.62	1.52	6.61	1.53	6.5[f]	
	6.76	1.06	6.77	1.07		

[a] Ref. 22; [b] Ref. 23; [c] Ref. 43; [d] Ref. 24; [e] Ref. 26; [f] Ref. 25.

experimental data. The predicted values are in principle vertical. However, due to the lack of observed vertical data, the semi-empirical parameters [1,2] have been obtained by a consequent fit to adiabatic IP's.

In view of this the agreement between the predicted IP of vinyl acetylene and the electron impact (EI) value [36] seems quite satisfactory. EI values are usually 0.1 – 0.4 eV higher than the corresponding adiabatic photoionization (PI) or photoelectron spectroscopy (PS) values (as for example illustrated by the phenyl acetylene data quoted in Table 3).[38]

There is further a very nice agreement between the predicted IP's of phenyl acetylene and the three PS potentials obtained by Turner.[37]

3. Charge distribution and dipole moments. The calculated atomic π-electron charges are given in Table 4. The deviations from uniform charge distribution are similar to those obtained earlier for butadiene and hexatriene.[1] They are a direct consequence of the use of different W_μ values for different atoms.

For the linear molecules, only the results obtained by method B are listed in the table, because method A gave identical results up to three decimal places.

The calculated π-electron dipole moment of VII is 0.37 (method A) and 0.36 D (method B), whereas the observed value is 0.43 D.[39] For IX the values are 0.28, 0.25, and 0.7 – 0.8 D,[40] in the same order.

4. Electronic spectra. The electronic transition energies were calculated by configurational mixing including all singly excited configurations. The oscillator strengths have been estimated from the formula of Mulliken and Rieke.[41]

The calculated values listed in Table 5 are the lowest singlet-singlet transition energies in each molecule, except for IV, V, and VI where only the lowest forbidden and the lowest allowed transition are included. Experimental values, when available, are given for comparison, and the overall agreement is seen to be satisfactory.

Table 5 demonstrates that methods A and B give essentially different results only in the case of certain symmetry-forbidden transitions, where the appropriate experimental data have not been analyzed. As an example, method A applied to acetylene predicts two $^1\Delta_u$ states (5.95 and 6.60 eV above the ground state), the energy difference being equal to the parameter $K_{\mu\nu}$. In method B where $K_{\mu\nu}=0$, these states are thus degenerate (5.88 eV). In the predicted spectra of the other molecules, the essential differences between the two methods are of the same nature.

On the basis of the observed acetylene spectrum, Mulliken [28] has estimated the absorption maximum of the transition $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^-$ to be near 5.7 eV, whereas T.M. Dunn suggests 6.5 eV.[28] Julg and Pellégatti [42] introduce certain correction terms to the measured adiabatic energy, resulting in 8.3 eV as an estimate of the vertical value. The present calculated energy, 5.99 or 6.08 eV, is in favour of Mulliken's estimate, especially as the maximum, as mentioned before, should be expected at a lower energy than the vertical value. This agreement is further an indirect support to the estimate 9.5 eV for the transition $^1\Sigma_g^+ \rightarrow {}^1\Sigma_u^+$, the only information from the acetylene spectrum that was used for parameter determination.

If the observed maximum at 7.2 eV is due to a $^1\Sigma_g^+ \rightarrow {}^1\Delta_u$ transition, as suggested by Mulliken,[28] the calculation method A would clearly be better than method B. The calculated value 6.60 eV would still be more than 0.6 eV

too low, however, as also this transition should have its vertical energy above the position of the absorption maximum. Any conclusive discussion of these questions is not possible until a successful analysis of the observed 7.2 eV bands has been performed.

The calculated symmetry-forbidden transitions of diacetylene are found in the same energy regions as the observed weak band systems. A closer comparison is not possible, however, until separate transitions are identified in these parts of the spectrum. The calculated value of the intense $^1\sum_g^+ \rightarrow {}^1\sum_u^+$ transition, 7.27 eV, suggests either an overlap with the strong Rydberg band at 7.5 eV, or alternatively that the supposed Rydberg state has π^* character, at least in part. In this connection it is of interest that the absorption bands of the higher polyacetylenes,[23] that seem analogous to the 7.5 eV Rydberg band, as already mentioned are described as due to $\pi - \pi^*$ transitions.[30] Furthermore, the original analysis of Rydberg bands [17,22] in the diacetylene spectrum does not seem quite correct, as the resulting IP of 10.79 eV is in conflict with the value now accepted, 10.2 eV.[16]

In the calculated spectrum of each polyacetylene, there is one transition with a very high oscillator strength. For the molecules I, III, and IV this transition was used for parameter determination, for II and V there was no appropriate experimental data, and for VI there was a similar agreement with the observed spectrum [23] as for III and IV. The very high oscillator strengths are parallelled by the very high observed extinction coefficients also listed in Table 5.

The weaker polyacetylene absorption, described as ranging from 7.2 to 3.2 eV (molecules I – VI) in an earlier section, remains a problem not only for the molecules I and II. Table 5 demonstrates that the lowest calculated transition energy for each molecule, is decreasing more slowly through the series than these observed values.

The UV spectrum of vinyl acetylene has been measured in isooctane solution.[43] The energy value quoted in Table 5 is the mean of the two strongest bands in a vibrational progression, and the agreement with calculation seems very good. However, when solvent effects are taken into account, this agreement is probably reduced by roughly 0.2 eV. The corresponding 5 eV bands of divinyl acetylene are shifted to lower energy by this amount when going from isooctane solution [43] to the gas phase spectrum (see below).

Price and Walsh measured the vacuum UV spectrum of divinyl acetylene.[24] The first observed energy value listed in Table 5, which was used for parameter determination, is the mean of the two strongest bands in a vibrational progression. The value 6.9 eV is a rough estimate of a broad maximum from their published plate. The calculated energies are in good agreement with these data.

The observed energies listed in Table 5 for phenyl acetylene are absorption maxima as estimated from a vacuum UV spectrum,[25] showing absorption only above 5.2 eV, and from a spectrum in hexane solution [26] covering the region 4.4 – 5.5 eV. Two of the values were used for parameter determination and the third is also in satisfactory agreement with the calculated spectrum.

CONCLUDING REMARKS

In the present work a calculation scheme that was earlier applied to conjugated double-bond systems,[1,2] has been extended so as to include the carbon-carbon triple bond. Two versions of the parameter scheme were developed, differing only in the treatment of the one-center exchange integral $K_{\mu\nu}$. The results given demonstrate the same satisfactory agreement with observed data as in the previous papers. A reservation must be made for the lowest excited singlet states of acetylene and the polyacetylenes, where more work is needed in the analysis of observed spectra as well as in theoretical calculations, in order to reach any definite conslusions. Here also the only essential differences were obtained in the predictions resulting from the two parameter versions.

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