286. The Consequences of σ and π Conjugative Interactions in Mono-, Di- and Triacetylenes

A Photoelectron Spectroscopic Investigation

by **Franz Brogli, Edgar Heilbronner**[1]**, Jakob Wirz** and **Else Kloster-Jensen**[2]
Physikalisch-chemisches Institut der Universität Basel, Switzerland

Robert G. Bergman[3]**, K. Peter C. Vollhardt**[3][4] and **Arthur J. Ashe III**[5]

(6. X. 75)

Summary. The HeI photoelectron spectra of mono-, di-, and triacetylenes are presented. In these compounds the two-centre π-orbitals of the ethynyl groups conjugate with the π-orbitals of double bonds or benzene moieties, or with the *Walsh* orbitals of three-membered ring systems. Assuming the validity of *Koopmans'* approximation, the observed energies of the radical cation states reached by electron ejection from π-orbitals can be rationalized in terms of a simple LCBO-MO model in those cases, where the molecule is planar. The corresponding numerical results for the ionization energies are in excellent agreement with experiment, if the three parameters of the model are properly calibrated. In contrast, the bands assigned to ejection from in plane π-orbitals are shifted to lower energies by *ca.* 0.5 eV with respect to the expectation values derived from the above model, due to 'through-bond' interaction with lower lying σ-orbitals.

Extensive σ/π mixing occurs in the non planar compounds for all orbitals. The assignments of the spectra of diethynylmethane, 1,4-hexadiyne, 1,2-diethynylethane and of *cis*- and *trans*-diethynylcyclopropane are backed by semiempirical SCF calculations. The spectra of the *cis* and *trans* isomers of diethynylethyleneoxide and diethynylethylenesulfide are discussed by comparison with the corresponding hydrocarbons and with oxirane and thiirane respectively.

Finally, the following topics are considered in detail: (a) The effect of spin orbit coupling on the spectrum of 1-iodo-1-butyne-3-ene; (b) the effect of the essentially free internal rotation in divinylacetylene on the band shapes of its photoelectron spectrum and (c) the relationship between the conjugative properties of ethylenic π-orbitals and of the *Walsh*-orbitals of cyclopropane.

Considerable effort has been devoted to the chemical detection of electronic interactions through bonds and space in conjugated and unconjugated unsaturated systems. Thermolytic reactions of mono- and polyolefines have become an established research area in preparative and theoretical chemistry [1], as exemplified by *Cope*- and vinyl cyclopropane rearrangements, retro-*Diels Alder* reactions, electrocyclic rearrangements etc. More recently heat [2] and metal [3] mediated chemical interactions of acetylenic compounds have received increased attention in the synthesis of molecules of theoretical and synthetic interest. To gain further understanding about the nature of these interactions and the ground state electronic structure of some acetylenic substrates, an investigation of the photoelectron spectra of a series of σ/π-conjugated acetylenes was undertaken.

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[1] Author, to whom correspondence must be addressed.

[2] Permanent address: Department of Chemistry, University of Nslo, Norway.

[3] Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California.

[4] Department of Chemistry, University of California Berkeley, California.

[5] A. P. Sloan Fellow.

Previous photoelectron-spectroscopic investigations on conjugated, unsaturated compounds [4], in particular on butadiene (**1**) [4], *cis*- and *trans*-1,3,5-hexatriene (**2**), diacetylene (**3** = 1,3-butadiyne) [4] [5] and triacetylene (**4** = 1,3,5-hexatriyne) [5] have shown that a LCBO-model (= Linear Combination of Bond Orbitals) yields an adequate approximation of the canonical π-orbitals of these compounds and thus, assuming the validity of *Koopmans'* theorem

$$I_{v,j} = -\varepsilon_j \tag{1}$$

($I_{v,j}$ = vertical ionization energy; ε_j = orbital energy) of their photoelectron spectra. If π_d stands for a double-bond and π_t for a triple-bond two-centre π-orbital, calibration of the matrix elements

$$\begin{aligned} A_d &= \langle\pi_d|\mathcal{H}|\pi_d\rangle\ ;\ A_t = \langle\pi_t|\mathcal{H}|\pi_t\rangle \\ B_d &= \langle\pi_d|\mathcal{H}|\pi_{d'}\rangle;\ B_t = \langle\pi_t|\mathcal{H}|\pi_{t'}\rangle \end{aligned} \tag{2}$$

(d, d' and t, t' linked π-orbitals), yields in a first approximation the following mean values [4] [5]:

$$\begin{aligned} A_d^0 &= -10.1\ \text{eV};\ A_t^0 = -11.4\ \text{eV} \\ B_d^0 &= -1.22\ \text{eV};\ B_t^0 = -1.23\ \text{eV} \end{aligned} \tag{3}$$

These mean self-energies A_d^0 and A_t^0 are approximately valid for both terminal and inner π-bonds. However, a more detailed analysis reveals that slightly differing basis energies must be assigned to both types of bonds if optimal agreement with the experimental data is to be obtained, or that antibonding orbitals π_d^*, π_t^* must be taken into consideration [4–6]. Within the limits of error we have $B_d^0 = B_t^0$; therefore it seems safe to assume that

$$B_{dt}^0 = \langle\pi_d|\mathcal{H}|\pi_t\rangle = -1.22\ \text{eV} \tag{4}$$

is a reasonable approximation for the resonance integral between a double-bond and a triple-bond two-centre π-orbital.

We shall now use the naive model embodied in formulae (1) to (4) as a start, to analyse the photoelectron spectra of vinylacetylene (**5** = 1-buten-3-yne) [7], divinylacetylene (**7** = 1,5-hexadiene-3-yne), *cis*- and *trans*-diethynylethylene (**8**, **9** = *cis*-, *trans*-3-hexen-1,5-diyne), of *o*-(**10**), *m*-(**11**) and *p*-diethynylbenzene (**12**) and of 1,3,5-triethynylbenzene (**13**) shown in Fig. 1, 2 and 3. The positions of the individual bands ⓙ are characterized by the adiabatic ionization energies $I_{a,j}$, *i.e.* the onset of the band ⓙ and by the position $I_{m,j}$ of the band maximum which, for all practical purposes, can be identified, within the limits of error, with the vertical ionization energy: $I_{v,j} \approx I_{m,j}$. The numbering ⓙ of the bands in the individual spectra does not imply a correlation. Wherever possible the spacing $\tilde{\nu}$ (in cm^{-1}) of the dominating vibrational fine-structure progression(s) is given. These data are collected in Table 1.

Using the self-energies A_d^0 and A_t^0 given in (3) and the resonance integral B_{dt}^0 of (4), we obtain for the orbital energies of the out-of-plane π-system of **5** [7] the values

$$\begin{aligned} \varepsilon\,(2a'') &= -\ \ 9.37\ \text{eV};\ (I_{v,1} = \ \ 9.58\ \text{eV}) \\ \varepsilon\,(1a'') &= -12.13\ \text{eV};\ (I_{v,3} = 12.00\ \text{eV}) \end{aligned} \tag{5}$$

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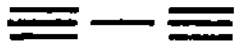

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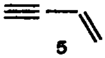

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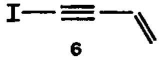

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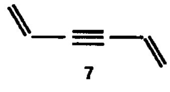

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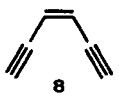

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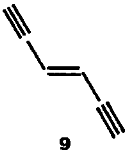

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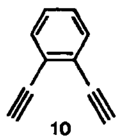

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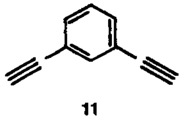

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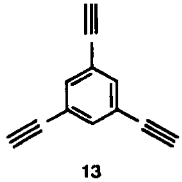

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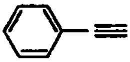

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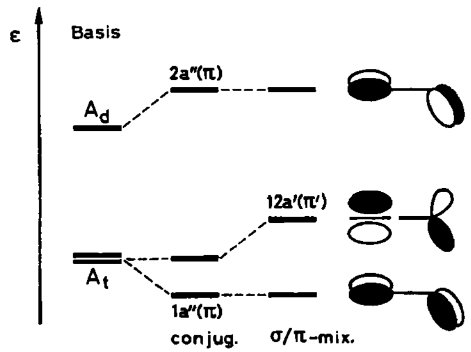
which are seen to be in excellent agreement with the observed band positions ($I_{v,1} = 9.6_3$ eV, $I_{v,3} = 12.0_1$ eV in [7]). Therefore the remaining π-band at $I_{v,2} = 10.58$ eV (10.6_1 eV in [7]) must be assigned to the in-plane π-orbital 12a′ (π′) which one might have expected to lie at $-A_t^0 = 11.4$ eV (Here and subsequently the in-plane π-orbitals are designated as π′). Obviously, the corresponding orbital energy ε (12a′) has been destabilized by 11.4 – 10.58 = 0.82 eV due to the interaction with those lower lying σ-orbitals which belong to the same irreducible representation A′, in particular with the CC-σ-bond orbital of the vinyl group and the CH-σ-bond orbital in position α to the triple bond:



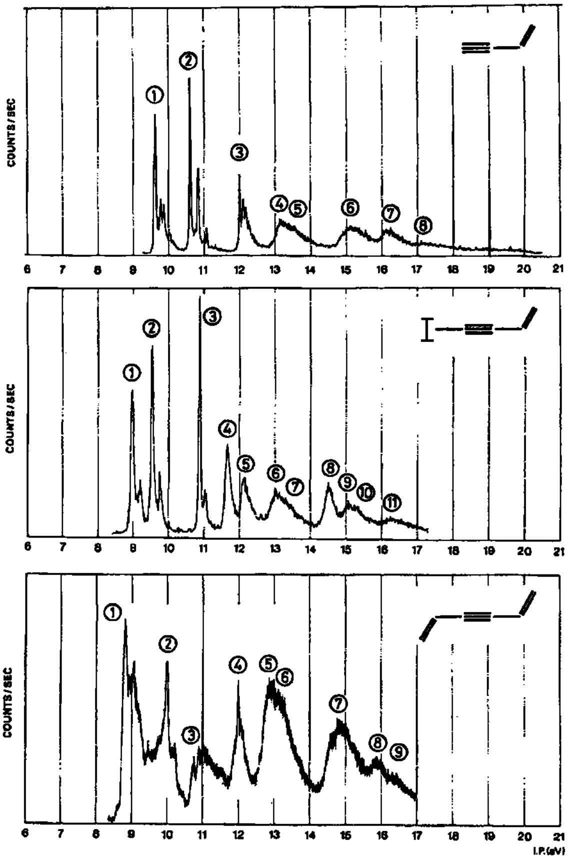


Fig. 1. *He(I) photoelectron-spectra of compounds* **5**, **6** *and* **7**

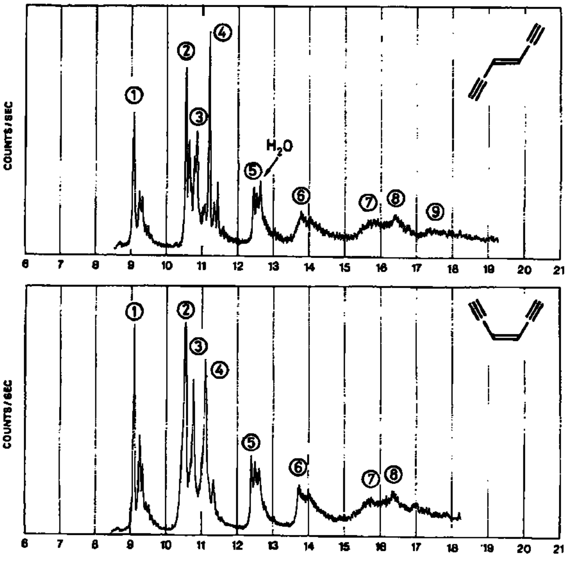


Fig. 2. *He(I)- photoelectron spectra of compounds* **8** *and* **9**

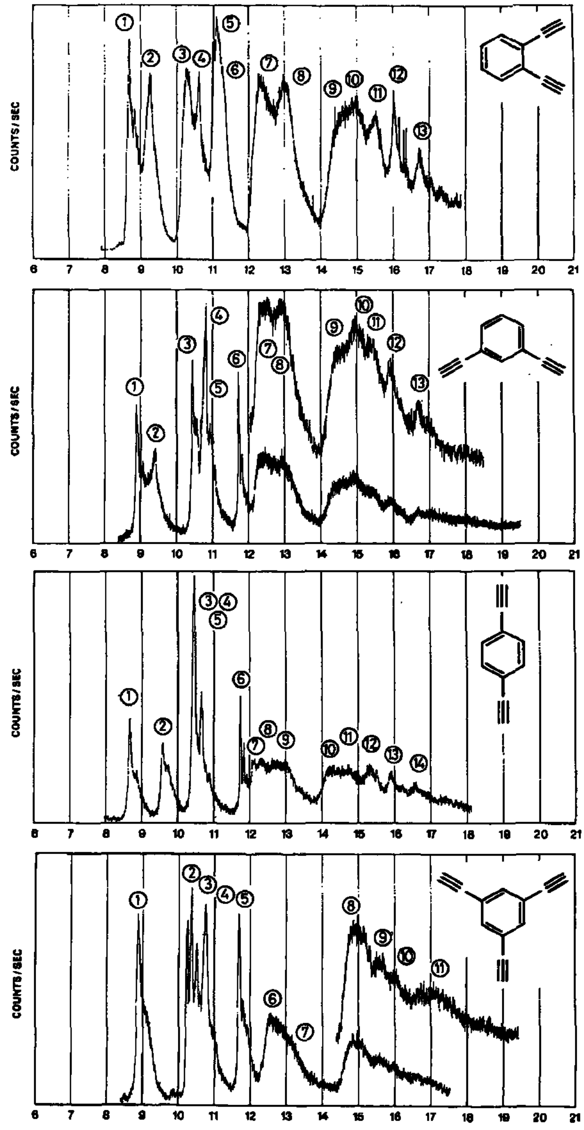


Fig. 3. *He(I) photoelectron spectra of compounds* **10**, **11**, **12** *and* **13**

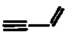
This assumption is supported by the results of an STO-3G *ab-initio* calculation due to *Radom & Pople* [8] and by those derived from a SPINDO-model [9] (see table 2 and the discussion of the results obtained for **8** and **9**).

Applying the simple LCBO model with parameters (3) and (4) to the *cis*- and *trans*-diethynylethylenes **8** and **9** one obtains by solving the 3 × 3-determinant for the out-of-plane π-system the following orbital energies:

$$\begin{array}{lll} & \mathbf{8}\ (cis);\ \mathbf{9}\ (trans) & \mathbf{8}\ (cis);\ \mathbf{9}\ (trans) \\ \varepsilon\,(2b_1;\ 2a_u) = & -\ 8.91\ \text{eV}; & (I_{v,1} = \ \ 9.10;\ \ 9.07\ \text{eV}) \\ \varepsilon\,(1a_2;\ 1b_g) = & -11.40\ \text{eV}; & (I_{v,4} = 11.1\ \ ;\ 11.18\ \text{eV}) \\ \varepsilon\,(1b_1;\ 1a_u) = & -12.59\ \text{eV}; & (I_{v,5} = 12.39;\ 12.43\ \text{eV}) \end{array} \qquad (6)$$

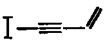
Table 1. *Experimental adiabatic* ($I_{a,j}$) *and vertical* ($I_{v,j}$) *ionization energies and spacing* $\tilde{\nu}$ *of the dominant vibrational fine structure of compounds* **5** *to* **13**

5 {C_s}



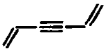
Band	I_a (eV)	I_v[a)] (eV)	$\tilde{\nu}$, Remarks (cm^{-1})	Assignment
①	9.58	9.58	2020, 1300	$2a''(\pi)$
②	10.58	10.58	1940, 1170	$12a'(\pi')$
③	12.00	12.00	1370, 760	$1a''(\pi)$
④	12.8	13.2		$11a'$
		(13.5)	shoulder	
⑤	14.8	15.2		$10a'$
⑥		16.1_5		$9a'$
⑦		17.4		$8a'(2s)$

6 {C_s}



Band	I_a (eV)	I_v[a)] (eV)	$\tilde{\nu}$, Remarks (cm^{-1})	Assignment
①	8.94	8.94	1860	$6a''(\pi)$
②	9.51	9.51	1800	$34a'(\pi')$
③	10.88	10.88	1370	$5a''(\pi)$
④		11.68		$33a'(\pi')$
⑤		12.1_5		$4a''(\pi)$
⑥		13.1_0		
⑦		13.4	shoulder	
⑧		14.5_5		

7 {C_{2h}} (assumed)

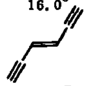


Band	I_a (eV)	I_v[a)] (eV)	$\tilde{\nu}$, Remarks (cm^{-1})	Assignment
①	8.50	8.71	1940, 1240	$2a_u(\pi)$
②		9.97	2050	$9b_u(\pi')$
③	10.72	11.00	1160	$1b_g(\pi)$
④		12.01		$1a_u(\pi)$
⑤		12.9_5		$9a_g$
⑥		13.2_5		$8b_u$
⑦		14.9_5		$8a_g$, $7b_u$
⑧		16.0		$7a_g$

8 {C_{2v}}

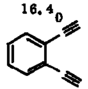
Band	I_a (eV)	I_v[a)] (eV)	$\tilde{\nu}$, Remarks (cm^{-1})	Assignment
①	9.10	9.10	2140, 1450	$2b_1(\pi)$
②		10.54		$9a_1(\pi')$
③		10.78		$8b_2(\pi')$
④		11.10	1950	$1a_2(\pi)$
⑤	12.39	12.39	900	$1b_1(\pi)$
⑥	13.6_5	13.74		$7b_2$
⑦	15.2	15.70		$8a_1$, $7a_1$
⑧		16.4_0		$6b_2$

9 {C_{2h}}



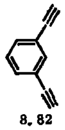
Band	I_a (eV)	I_v[a)] (eV)	$\tilde{\nu}$, Remarks (cm^{-1})	Assignment
①	9.07	9.07	2060, 1370	$2a_u(\pi)$
②	10.55	10.55	1170, 780	$9a_g(\pi')$
③		10.85	1450 ?	$8b_u(\pi')$
④	11.18	11.18	2020, 1170	$1b_g(\pi)$
⑤	12.43	12.43	680	$1a_u(\pi)$
⑥	13.5_0	13.7_5		$8a_g$
⑦	15.2	15.7_5		$7a_g$, $7b_u$
⑧		16.4		$6a_g$

10 {C_{2v}}



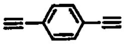
Band	I_a (eV)	I_v[a)] (eV)	$\tilde{\nu}$, Remarks (cm^{-1})	Assignment
①	8.69	8.69	1250	$3b_1$
②		9.25		$2a_2$
③		10.26		$15a_1(\pi')$
④	9.9	10.58		$13b_2(\pi')$
⑤	10.98	10.98		$1a_2(\pi)$
⑥		11.10		$2b_1(\pi)$
⑦		12.24		(σ)
⑧		12.9_0		$1b_1(\pi)$

11 {C_{2v}}



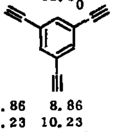
Band	I_a (eV)	I_v[a)] (eV)	$\tilde{\nu}$, Remarks (cm^{-1})	Assignment
①	8.82	8.82	1130	$2a_2$
②		9.30	650	$3b_1$
③	10.37	10.37	1130	(π')
④,⑤		10.72	650	$2b_1(\pi)$; (π')
⑥	11.65	11.65		$1a_2(\pi)$
⑦		12.5_0		(σ)
⑧		12.9_0		$1b_1(\pi)$

12 {D_{2h}}



Band	I_a (eV)	I_v[a)] (eV)	$\tilde{\nu}$, Remarks (cm^{-1})	Assignment
①	8.58	8.58	1450, 360	$2b_{2g}$
②	9.54	9.54	1050	$1b_{1g}$
③,④	10.43	10.43	1770	$2b_{3u}(\pi)$
⑤		10.65		$4b_{3g}(\pi')$; $5b_{2u}(\pi')$
⑥	11.74	11.74		$1b_{2g}(\pi)$
⑦		12.12		(σ)
⑧		12.3_5		(σ)

13 {D_{3h}}



Band	I_a (eV)	I_v[a)] (eV)	$\tilde{\nu}$, Remarks (cm^{-1})	Assignment
①	8.86	8.86		$2e''$
②	10.23	10.23		$2a''_2(\pi)$
③	10.35 10.51	10.35 10.51		$2a'_2(\pi')$
④		10.84		$11e'(\pi')$
⑤		11.68		$1e''(\pi)$
⑥		12.5_5		(σ)
⑦		12.9_5	*shoulder*	$1a''_2(\pi)$

a) The PE.-spectra have been calibrated *in situ* with Ar, Xe and benzene (HeIα and β lines). Where two full decimals are given the ionization energies are correct to + 0.02 eV; the vibrational spacings may be in error by ± 80 cm^{-1}.

The good agreement with the experimental values found for the bands ①, ④ and ⑥ leaves no doubt that the two remaining bands ②, ③ in the range 10.5 to 11 eV (see

Table 2. *Calculated orbital energies* ε_j *for compounds* **5**, **7**, **8** *and* **9**

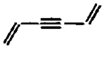
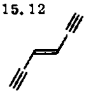
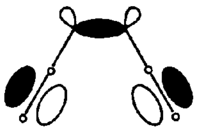
Orb.	SPINDO - ε (eV)	STO 3G - ε (eV)	Description	Orb.	SPINDO - ε (eV)	MINDO/2 - ε (eV)	CNDO/2 - ε (eV)	Description
5 $\{C_s\}$				8 $\{C_{2v}\}$				
2a''	9.61	7.71 [8]	π_-	$2b_1$	9.22	9.16	12.69	π_+
12a'	10.32	9.10	π'	$9a_1$	10.28	10.23	15.10	π_-' (100 % π')
1a''	11.57	11.13	π_+	$8b_2$	10.28	10.35	15.48	π_+' (92 % π')
11a'	12.69	13.39	σ (CH_2)	$1a_2$	10.63	11.01	17.96	π_- (100 % π_t)
10a'	14.68	15.02	σ	$1b_1$	12.02	12.71	22.14	π_+ (56 % π_d)
9a'	15.77	16.79	σ	$7b_2$	13.28	11.11	16.82	σ (vinyl)
8a'	16.60	18.17	2s(C)	$8a_1$	15.12	12.18	20.60	
7 $\{C_{2h}\}$(assumed)				9 $\{C_{2h}\}$				
$2a_u$	9.11	6.79 [8]	π_u	$2a_u$	9.28	9.14	12.62	π_+
$9b_u$	10.02	8.76	π_u'	$9a_g$	10.37	10.13	14.85	π' (92 % π')
$1b_g$	10.67	9.62	π_g	$8b_u$	10.50	10.56	16.36	π' (98 % π')
$1a_u$	11.90	11.62	π_u	$1b_g$	10.83	11.14	18.21	π_- (100 % π_t)
$9a_g$	12.52	13.07	σ	$1a_u$	12.06	12.69	22.02	π_+ (53 % π_d)
$8b_u$	12.84	13.53	σ (CH_2)	$8a_g$	13.14	11.00	16.14	σ (vinyl)
$8a_g$	14.52	14.71	σ (CC)	$7a_g$	15.18	13.14	21.68	
$7b_u$	14.88			$7b_u$	15.85	13.43	21.65	
$7a_g$	15.93			$6a_g$	16.58	16.94	23.49	

Fig. 2) are due to electron ejection from the in-plane π-orbitals which are dominated by the linear combinations

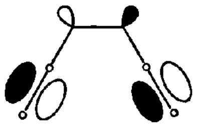
$$
\begin{array}{lll}
 & \mathbf{8}\ (cis); & \mathbf{9}\ (trans) \\
\pi'_{t-} = (\pi'_t - \pi'_{t'}) \,/\, \sqrt{2}: & 8b_2(\pi'); & 8b_u(\pi') \\
\pi'_{t+} = (\pi'_t + \pi'_{t'}) \,/\, \sqrt{2}: & 9a_1(\pi'); & 9a_g(\pi')
\end{array}
\tag{7}
$$

both of which are destabilized with respect to $A_t^0 = -11.4$ eV, as a result of interaction with σ-orbitals belonging to the irreducible representations A_1 and B_2 (in **8**) or A_g and B_u (in **9**). In fact, the observed band positions are $I_{v,2} = -10.5_5$ eV (**8**, **9**) and $I_{v,3} = -10.7_5$ (**8**), -10.8_5 (**9**) eV. Qualitatively we would expect that the lower ionization energy $I_{v,2}$ has to be correlated with the orbitals $9a_1(\pi')$ and $9a_g(\pi')$ because of the availability of the central CC-σ-bond orbital for 'through-bond' interaction [10] [11]:

8

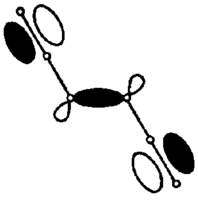


$9a_1(\pi)$

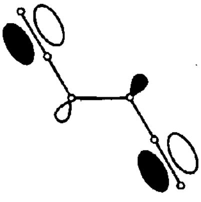


$8b_2(\pi)$

9



$9a_g(\pi)$



$8b_u(\pi)$

In table 2 are given the results of SPINDO [9], MINDO/2 [12] and CNDO/2 [13] calculations for **8** and **9**, assuming standard geometries for these molecules. It should be noted that the latter two models tend to give too high lying σ-orbitals within the manifold of the π-orbitals. If this artifact is disregarded, then the agreement with the orbital sequence derived from our simple LCBO-model is perfect for all three treatments. The pictorial representations [14] of the five π-orbitals (as obtained from the SPINDO treatment) of **8** and **9** shown in Fig. 4 support our previous argument concerning the 'through-bond' interaction between the terminal in-plane π-orbitals $\pi'_t, \pi'_{t'}$. It is obvious that in $9a_1(\pi')$ of **8** and in $9a_g(\pi')$ of **9** the basis orbitals $\pi'_t, \pi'_{t'}$, use the orbital of the central CC-σ-bond as an effective relay-orbital for 'through-bond' interaction. However, a more detailed analysis of the calculated orbitals and of their energies indicates that in the *cis*-configurated molecule **8** 'through-space' interaction between π'_t and $\pi'_{t'}$ is rather significant, as suggested by the accidental equality of the orbital energies of $9a_1(\pi')$ and $8b_2(\pi')$.

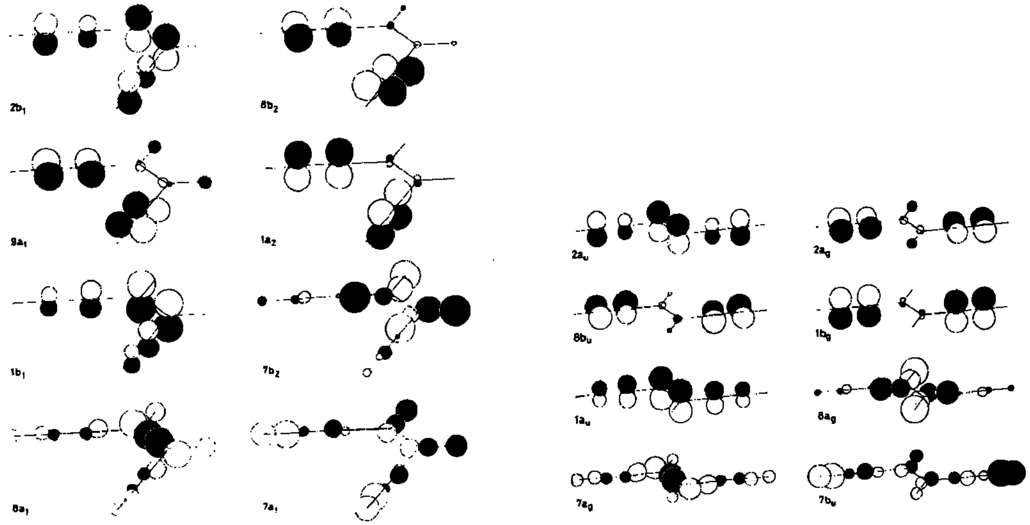


Fig. 4. *Molecular orbital* (SPINDO) *of compounds* **8** *and* **9**. Starting with the highest occupied orbital in the upper left-hand corner, reading from left to right and top to bottom

At this stage it is of advantage to adapt our model to the systems **8** and **9** by introducing slight changes in the self-energies A_d^0 and A_t^0 (3) and to check the value of B_{dt}^0 (4). Using the experimental data for **8** and **9** in conjunction with the approximation (1) we find the new set of parameters (8) by solving the corresponding secular determinants in reverse, in order to obtain optimal agreement with the experimental band positions $I_{v,j}$. This yields:

$$\begin{aligned} A_d &= -10.35\ \text{eV};\quad A_t = -11.15\ \text{eV} \\ B_{dt} &= -\ \ 1.14\ \text{eV} \end{aligned} \tag{8}$$

As can be seen these values do not differ materially from those used above. In particular it is found that in the context of our simple LCBO model our assumption

$B^0_d = B^0_t = B^0_{dt}$ was a reasonable one. Using the parameter set (8) we obtain for the molecules discussed so far:

$$\begin{array}{lll} \mathbf{5}: & \varepsilon(2a'') = -\ \ 9.54\ \text{eV} & (I_{v,1} = \ \ 9.58\ \text{eV}) \\ & \varepsilon(1a'') = -11.96\ \text{eV} & (I_{v,2} = 12.00\ \text{eV}) \\ \mathbf{8}: & \varepsilon(2b_1) = -\ \ 9.09\ \text{eV} & (I_{v,1} = \ \ 9.10\ \text{eV}) \\ & \varepsilon(1a_2) = -11.15\ \text{eV} & (I_{v,4} = 11.1\ \ \text{eV}) \\ & \varepsilon(1b_1) = -12.41\ \text{eV} & (I_{v,5} = 12.39\ \text{eV}) \\ \mathbf{9}: & \varepsilon(2a_u) = -\ \ 9.09\ \text{eV} & (I_{v,1} = \ \ 9.07\ \text{eV}) \\ & \varepsilon(1b_g) = -11.15\ \text{eV} & (I_{v,4} = 11.18\ \text{eV}) \\ & \varepsilon(1a_u) = -12.41\ \text{eV} & (I_{v,5} = 12.43\ \text{eV}) \end{array} \qquad (9)$$

Assuming that 'through-space' interaction between π'_t and $\pi'_{t'}$ could be neglected, electron ejection from the in-plane π-orbitals would be expected to yield bands in positions $I_V = -A_t = 11.15$ eV. However, these bands occur at lower ionization energies, which implies that the corresponding π'-orbitals have been destabilized by $\tau = -A_t - I_V$ eV due to 'through-bond' interaction:

$$\begin{array}{lll} \mathbf{5} & \tau \ = \delta\varepsilon(12a') & = 0.57\ \text{eV} \\ \mathbf{8} & \tau_+ = \delta\varepsilon(\ 9a_1) & = 0.61\ \text{eV} \\ & \tau_- = \delta\varepsilon(\ 8b_2) & = 0.37\ \text{eV} \\ \mathbf{9} & \tau_+ = \delta\varepsilon(\ 9a_g) & = 0.60\ \text{eV} \\ & \tau_- = \delta\varepsilon(\ 8b_u) & = 0.30\ \text{eV} \end{array} \qquad (10)$$

The surprising observation that τ_+ and τ_- are respectively the same in **8** and **9**, is presumably due to a fortuitous compensation of increased 'through-space' and decreased 'through-bond' interactions between π'_t and $\pi'_{t'}$ in the *cis*-configurated compound **8**, relative to **9**.

A first test of the adjusted parameter set (8) is provided by 1-iodo-3-buten-1-yne (**6**) (the iodo derivative of **5**). In this case the in-plane and out-of-plane π-orbitals encompass the two doubly occupied p-atomic orbitals 5p′ and 5p of the iodine atom. Previous investigations of the photoelectron spectra of halo- and dihaloacetylenes [15] yielded a basis orbital energy $A_I = -10.6$ eV for the 5p-orbitals of an iodine atom attached to a triple bond. The corresponding resonance integral for their conjugation with the triple bond π-orbitals π_t, π'_t was found to be $B_{I,t} = -1.0$ eV. As a consequence of the presence of a heavy atom, spin-orbit coupling is expected to lead to sizeable splits and/or shifts of some of the π-bands [15, 16]. Because **6** belongs only to the symmetry group C_s, one has to take into account the competition that exists between the local spin-orbit interaction at the heavy iodine atom, characterized in this case by its spin-orbit interaction constant $\zeta = 0.6$ eV, and the different degree of conjugation of the 5p′ and 5p atomic orbitals with the in-plane and out-of-plane π-orbitals of the alkyl moiety. To a first approximation this problem can be handled in the framework of a simple independent electron treatment [16] which demands the diagonalization of the following matrix for the case of the π-system of **6**:

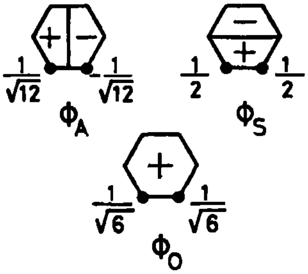
$$\begin{pmatrix} A_I & -i\zeta/2 & B_{I,t} & 0 & 0 \\ i\zeta/2 & A_I & 0 & 0 & B_{I,t} \\ B_{I,t} & 0 & A_t & B_{dt} & 0 \\ 0 & 0 & B_{dt} & A_d & 0 \\ 0 & B_{I,t} & 0 & 0 & A_{t'} \end{pmatrix} \qquad (11)$$

With the parameters previously defined we obtain from (11) the following eigenvalues ε, which are compared to the observed vertical ionization energies of the bands ① to ⑤ (see Fig. 1):

$$\begin{array}{ll} \varepsilon_1\,(\ 6a'') = -\ \ 9.22\ \text{eV} & I_{v,1} = \ \ 8.94\ \text{eV} \\ \varepsilon_2\,(34a'\,) = -\ \ 9.81\ \text{eV} & I_{v,2} = \ \ 9.51\ \text{eV} \\ \varepsilon_3\,(\ 5a'') = -10.53\ \text{eV} & I_{v,3} = 10.88\ \text{eV} \\ \varepsilon_4\,(33a'\,) = -11.91\ \text{eV} & I_{v,4} = 11.7\ \ \text{eV} \\ \varepsilon_5\,(\ 4a'') = -12.38\ \text{eV} & I_{v,5} = 12.2\ \ \text{eV} \end{array} \qquad (12)$$

In view of the rather simple model and considering the neglect of second order spin orbit coupling which is rather important in iodo compounds [17] the result is quite respectable. It should be noted that the labels A′ and A″ of the irreducible representations of C_s are not really adequate under conditions of strong spin orbit coupling, but can nevertheless be used in a meaningful way in the present case. The most important result of our treatment is that the gap $I_{v,2} - I_{v,1} = 0.57$ eV is faithfully reproduced, *i.e.* $\varepsilon_2 - \varepsilon_1 = 0.59$ eV. This is within the limits of error the value of ζ. However, in agreement with previous observations [16], it would be erroneous to interpret this result as indicating that the particular orbital is completely localized on the iodine atom: The (near) equivalence $I_{v,2} - I_{v,1} = \zeta$ is due to the compensation of the decreased spin-orbit coupling contribution to the split between bands ① and ② by an increased conjugation induced splitting. (For details see [16]).

A further verification of our naive LCBO model is provided by the data for ethynylbenzene (**14** = phenylacetylene) [18], *o*-, *m*-, *p*-diethynylbenzene (**10, 11, 12**) and for 1,3,5-triethynylbenzene (**13**). There the π_d-basis orbital of **8** and **9** has to be replaced by the set of three benzene orbitals



(13)

the self-energies A_ξ (ξ = A, S, 0) of which are assigned the following values

$$\begin{aligned} A_A = \langle\phi_A|\mathcal{H}|\phi_A\rangle = A_S = \langle\phi_S|\mathcal{H}|\phi_S\rangle &= -\ \ 9.25\ \text{eV} \\ A_O = \langle\phi_O|\mathcal{H}|\phi_O\rangle &= -12.25\ \text{eV}. \end{aligned} \qquad (14)$$

The interaction terms of the type

$$B_{\xi t} = \langle\phi_\xi|\mathcal{H}|\pi_t\rangle;\quad \xi = A, S, O \qquad (15)$$

can be derived from the value $B_{dt} = -1.14$ eV given in (8) by taking into account the change in the atomic orbital coefficients $c_{j\mu}$ at the point of substitution μ *i.e.* its value in ϕ_A, ϕ_S or ϕ_0 relative to the value $c_d = 1/\sqrt{2}$ in π_d:

$$\begin{array}{llll} & \mathbf{10} & \mathbf{11} & \mathbf{12} \\ A & +B_{dt}/\sqrt{6} & B_{dt}/\sqrt{6} & +B_{dt} \cdot \sqrt{2/3} \\ S & B_{dt}/\sqrt{2} & +B_{dt}/\sqrt{2} & 0 \\ 0 & B_{dt}/\sqrt{3} & B_{dt}\sqrt{3} & B_{dt}/\sqrt{3} \end{array} \qquad (16)$$

Solving the eigenvalue/eigenvector problems for the molecules **10** to **14** yields π-orbital energies ε_j for the out-of-plane π-systems, which are compared to the observed vertical ionization energies in (18). The basis orbitals listed in the square brackets are arranged according to decreasing importance of their contribution to the particular orbital. The symbols π_+, π_-, π_e and π_a refer to the linear combinations

$$\begin{aligned} \pi_+ &= (\pi_t + \pi_{t'})/\sqrt{2} \\ \pi_e &= \begin{cases} (2\pi_t - \pi_{t'} - \pi_{t''})/\sqrt{6} \\ (\pi_{t'} - \pi_{t''})/\sqrt{2} \end{cases} \\ \pi_a &= (\pi_t + \pi_{t'} + \pi_{t''})/\sqrt{3}. \end{aligned} \qquad (17)$$

All values are given in eV:

14: ethynylbenzene (= phenylacetylene)

$$\begin{array}{llll} \varepsilon(3b_1) = -\ 8.85 & I_{v,1} = \ 8.78\,[18] & [\phi_A, -\pi, \phi_0] \\ \varepsilon(1a_2) = -\ 9.25 & I_{v,2} = \ 9.48 & [\phi_S] \\ \varepsilon(2b_1) = -11.19 & I_{v,4} = 11.00 & [\pi, -\phi_0, \phi_A] \\ \varepsilon(1b_1) = -12.61 & I_{v,6} = 12.60 & [\phi_0, \pi, \phi_A] \end{array} \qquad (18)$$

10: *o*-diethynylbenzene

$$\begin{array}{lll} \varepsilon(3b_1) = -\ 8.67 & I_{v,1} = \ 8.69 & [\phi_S, -\pi, \phi_0] \\ \varepsilon(2a_2) = -\ 9.04 & I_{v,2} = \ 9.25 & [\phi_A, -\pi_-] \\ \varepsilon(2b_1) = -11.10 & I_{v,5} = 10.98 & [\pi_+, -\phi_0, \phi_S] \\ \varepsilon(1a_2) = -11.36 & I_{v,6} = 11.1 & [\pi_-, \phi_A] \\ \varepsilon(1b_1) = -12.88 & I_{v,8} = 12.9 & [\phi_0, \pi_+, \phi_S] \end{array}$$

11: *m*-diethynylbenzene

$$\begin{array}{lll} \varepsilon(2a_2) = -\ 8.72 & I_{v,1} = \ 8.82 & [\phi_S, -\pi_-] \\ \varepsilon(3b_1) = -\ 9.02 & I_{v,2} = \ 9.30 & [\phi_A, -\pi_+, \phi_0] \\ \varepsilon(2b_1) = -10.82 & I_{v,4} = 10.72 & [\phi_0, -\pi_+, -\phi_A] \\ \varepsilon(1a_2) = -11.68 & I_{v,6} = 11.65 & [\pi_-, \phi_S] \\ \varepsilon(1b_1) = -12.81 & I_{v,8} = 12.9 & [\phi_0, \pi_+, \phi_A] \end{array}$$

12: *p*-diethynylbenzene

$$\begin{array}{lll} \varepsilon(2b_{2g}) = -\ 8.58 & I_{v,1} = \ 8.58 & [\phi_A, -\pi_-] \\ \varepsilon(1b_{1g}) = -\ 9.25 & I_{v,2} = \ 9.54 & [\phi_S] \\ \varepsilon(2b_{3u}) = -10.62 & I_{v,3} = 10.43 & [\pi_+, -\phi_0] \\ \varepsilon(1b_{2g}) = -11.82 & I_{v,6} = 11.74 & [\pi_-, \phi_A] \\ \varepsilon(1b_{3u}) = -12.78 & I_{v,8} = 12.8 & [\phi_0, \pi_+] \end{array}$$

13: 1,3,5-triethynylbenzene

$$\begin{array}{lll}
\varepsilon(2e'') = -\ \ 8.72 & I_{v,1} = \ \ 8.86 & [\phi_e, -\pi_e] \\
\varepsilon(2a_2'') = -10.43 & I_{v,2} = 10.23 & [\pi_a, -\phi_0] \\
\varepsilon(1e'') = -11.68 & I_{v,5} = 11.68 & [\pi_e, \phi_e] \\
\varepsilon(1a_2'') = -12.97 & I_{v,7} = 13.0 & [\phi_0, \pi_a]
\end{array}$$

The expectation values for the orbital energies of the in-plane π-orbitals of **10**, **11**, **12** and **14** are estimated to be close to and perhaps slightly above those observed in the cases **5**, **8** and **9**. The highest occupied σ-orbitals of the benzene moiety are the pair of 'ribbon-orbitals' [19] derived from the e_{2g}-orbitals of benzene ($\varepsilon(e_{2g}) = -11.4$ eV) [20]. However, because the in-plane π'-orbitals π'_t and $\pi'_{t'}$ have rather low lying orbital energies, they will also interact significantly with deeper σ-orbitals of appropriate symmetry. Therefore it is rather difficult to derive meaningful estimates of the size of the 'through-bond' interactions, beyond the general statement mentioned at the beginning of this paragraph, which is borne out by the observed π'-band positions ($I_{v,j}$ in eV):

$$\begin{array}{lccccc}
 & \mathbf{10} & \mathbf{11} & \mathbf{12} & \mathbf{13} & \mathbf{14} \\
\pi'\text{-bands} \left\{ \begin{array}{l} \\ \\ \\ \end{array} \right. & \begin{array}{c} 10.26 \\ \\ 10.58 \end{array} & \begin{array}{c} 10.37 \\ \\ 10.72 \end{array} & \begin{array}{c} \\ \sim 10.7 \\ \\ \end{array} & \begin{array}{c} 10.35 \\ \\ 10.84 \end{array} & \begin{array}{c} \\ 10.28\ [18] \\ \\ \end{array}
\end{array} \qquad (19)$$

Finally, the last π-band in the spectra of the compounds **10** to **14** is preceeded by (a) σ-band(s), in close analogy to the situation encountered in the case of benzene.

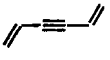
The excellent agreement between the extrapolated and the observed photoelectron spectra of **10** to **14** confirms once more that an LCBO model based on localized two-centre π-orbitals, which takes σ/π-mixing qualitatively into account, allows for a meaningful correlation of the spectra of unsaturated molecules, for which such a description would be expected to hold according to chemical intuition. Indeed the large number of photoelectron spectra of different molecules which can be effectively correlated with each other in this simple fashion, indicates that the assignments so obtained are as well established as those derived by the use of semi-empirical or *ab-initio* many-electron treatments. However, if σ/π-separation is no longer an adequate assumption, even to first order, the application of the LCBO-model becomes questionable and one has to rely on appropriate many-electron models. This is the case for the remaining systems to be discussed in this paper.

Divinylacetylene (=1,5-hexadiene-3-yne) (**7**) is a rather special case. As can be seen from the results summarized in Table 2, the vertical ionization energies taken from its photoelectron spectrum (Fig. 1) are well reproduced both by *ab-initio* [8] and by SPINDO-calculations, if one assumes an anti-planar conformation. However, one would expect that **7** in its closed-shell ground state should exhibit almost free internal rotation of the two vinyl groups, around their common C–C≡C–C axis. This is supported by the results of MINDO/3 [21] calculations which predict a barrier of only 0.4 kJ mol^{-1}, the anti- and synplanar conformations representing the minima of the bimodal potential function.

The question to be answered is, whether the assumption of free rotation in the ground state of **7** is compatible with the observed structure of the photoelectron-spectrum. In particular, it must be shown that there is no contradiction between the fact that on the one hand the positions $I_{v,j}$ of the observed maxima agree with the predictions derived from a rigid anti-planar conformation and, on the other hand, the assumption that we are in the presence of a continuum of conformations in which each twist angle ω is affected with approximately the same probability.

In Table 3 and in Fig. 5 are shown the orbital energies of **7** as a function of the twist angle ω, as derived from a SPINDO model. The rotational barrier of the radical cation 7^+ in its ground and first excited state can be roughly approximated by the angular dependence of the orbital energies $\varepsilon(2a_u) \rightarrow \varepsilon(10a_1)$ and $\varepsilon(9b_u) \rightarrow \varepsilon(2b_1)$. This is obviously a rather crude assumption, which does not however affect the qualitative result we are aiming at, namely the calculation of the *Franck-Condon* envelope to be expected under the above circumstances. To derive this envelope we proceed as follows (*cf.* [8]):

Table 3. *Angular dependence of (negative) orbital energies* $-\varepsilon_j$ *(eV) of* **7** *and* **17** *calculated according to the* SPINDO *method.* ω denotes the dihedral angle between the two vinyl groups in **7** and the two ethynyl groups in **17**



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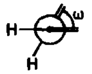
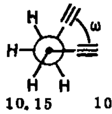


$\{C_{2v}\}$	0°	60°	90°	120°	180°	$\{C_{2h}\}$
$2b_1$	9.11	9.25	9.42	9.25	9.11	$2a_u$
$10a_1$	10.02	9.65	9.42	9.64	10.02	$9b_u$
$1a_2$	10.67	11.11	11.41	11.12	10.67	$1b_g$
$1b_1$	11.90	11.67	11.41	11.68	11.90	$1a_u$
$9a_1$	12.54	12.53	12.53	12.53	12.52	$9a_g$
$8b_2$	12.81	12.82	12.83	12.84	12.84	$8b_u$
$7b_2$	14.68	14.65	14.61	14.57	14.52	$8a_g$
$8a_1$	14.69	14.74	14.79	14.83	14.88	$7b_u$

(17),



$8b_2$	10.13	10.15	10.14	10.17	10.23	$9a_g$
$2a_2$	10.15	10.25	10.26	10.29	10.37	$2a_u$
$2b_1$	10.34	10.33	10.39	10.41	10.41	$2b_g$
$9a_1$	10.36	10.47	10.56	10.60	10.62	$8b_u$
$1a_2$	13.38	13.38	13.36	13.38	13.33	$1b_g$
$7b_2$	13.71	13.67	13.59	13.46	13.49	$8a_g$
$8a_1$	14.11	14.11	14.17	14.23	14.28	$7a_g$
$7a_1$	15.55	15.61	15.69	15.64	15.62	$7b_u$
$1b_1$	15.92	15.76	15.69	15.78	15.89	$1a_u$

The internal rotation ($0 \leqslant \omega \leqslant 2\pi$) of the two vinyl groups with respect to the C–C≡C–C axis is described by the solution of the *Schrödinger*-equation

$$\left[-\frac{\hbar^2}{2I'}\frac{d^2}{d\omega^2} + V(\omega)\right]\theta(\omega) = E\,\theta(\omega) \tag{20}$$

where I′ is the reduced moment of inertia for internal rotation. The potential V(ω) can be written as

$$V(\omega) = \frac{1}{2}\left[V_0 + \sum_{k=1}^{N} V_k \cos(k\omega)\right] \tag{21}$$

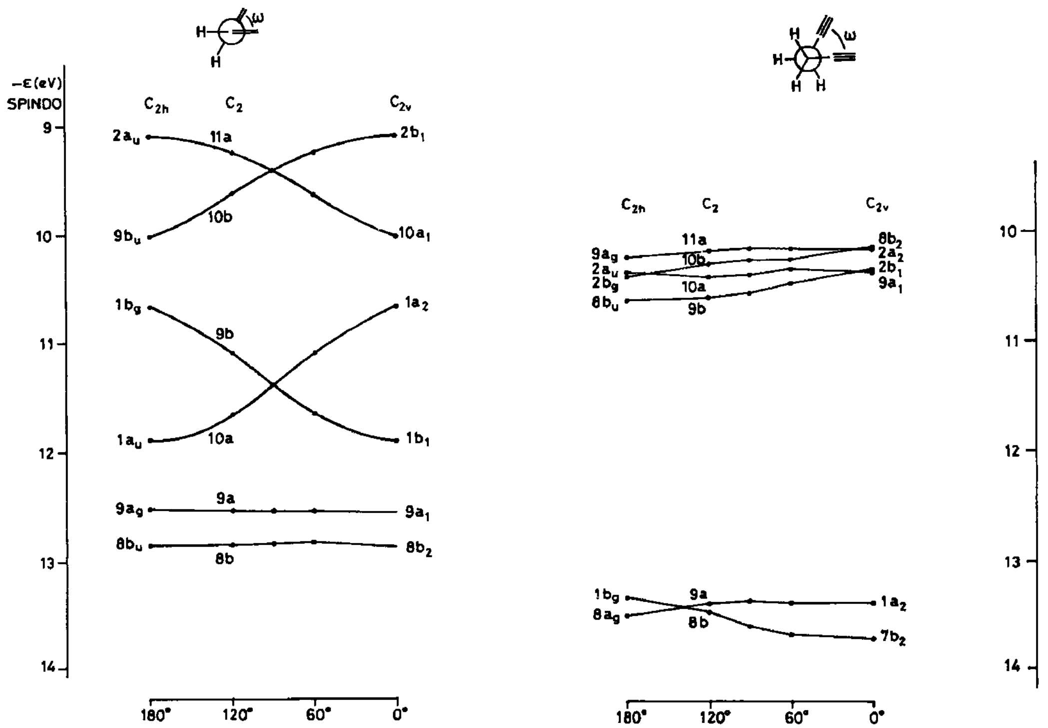


Fig. 5. *Angular dependence of molecular orbital energy* ε_j *of* **7** (left) *and* **17** (right). ω denotes the dihedral angle between the two vinyl or the two ethynyl groups

For the closed shell ground state of **7** we have explored the range of potentials $V''(\omega)$ with $0 \leqslant V''_0 \leqslant 700\ \text{cm}^{-1}$, $V''_1 = -V''_0$, $N = 1$. For the ground state of the radical cation 7^+ we obtain from the data of Table 3 and Fig. 5 the values $V'_0 = 6050\ \text{cm}^{-1}$, $V'_1 = 6990\ \text{cm}^{-1}$, $V'_2 = 1291\ \text{cm}^{-1}$, $V'_3 = 350\ \text{cm}^{-1}$ with $N = 3$. These parameters define the potential $V'(\omega)$ going from $\varepsilon(10a_1)$ $(\omega = 0)$ to $\varepsilon(2a_u)$ $(\omega = \pi)$ and back $(\pi \leqslant \omega \leqslant 2\pi)$. The potential for $\varepsilon(2b_1)$ $(\omega = 0)$ to $\varepsilon(9b_u)$ $(\omega = \pi)$ differs from the previous one by a phase-shift of π. Therefore it is sufficient to take only one of the radical cation potentials into account for the calculation of the *Franck-Condon* envelope. To solve (20) with $V(\omega) = V''(\omega)$ or $V(\omega) = V'(\omega)$ we expand $\theta(\omega)$ in a *Fourier*-series, *i.e.*

$$\theta_S(\omega) = \mathcal{N}_S \sum_{l=0}^{M} a_l \cos(l\omega)\ , \qquad \theta_A(\omega) = \mathcal{N}_A \sum_{l=1}^{M} b_l \sin(l\omega) \qquad (22)$$

depending on whether $\theta(\omega)$ is symmetric (S) or antisymmetric (A). Because of the large size of the reduced moment of inertia I', the rotational energy levels E''_i of the molecule **7** in its electronic ground state are closely spaced. Their population is proportional to the *Boltzmann* factor $\exp(\Delta E''_i/kT)$ with $\Delta E''_i = E''_i - E''_0$. The transition probabilities between two levels E''_i and E'_j can be written in terms of the coefficients a''_{il}, a'_{jl} or b''_{il}, b'_{jl} of the solutions $\theta_{S,i}$, $\theta_{S,j}$ or $\theta_{A,i}$, $\theta_{A,j}$ of (20) (see formulae (22)) in the following form

$$P_{S,i\rightarrow j} \propto \exp(\Delta E''_i/kT) \sum_{l=0}^{M} a''_{il}\, a'_{jl}\ , \qquad P_{A,i\rightarrow j} \propto \exp(\Delta E''_i/kT) \sum_{l=1}^{M} b''_{il}\, b'_{jl} \qquad (23)$$

To obtain a graphical representation of the *Franck-Condon* envelope, each transition $i \to j$ is assigned a *Lorentzian* curve of halfwidth 160 cm^{-1}, *i.e.* the resolution of our instrument, a peak height proportional to $P_{S,i\to j}$ or $P_{A,i\to j}$ and a position of $E'_j - E''_i$ relative to an arbitrary zero. The result is shown in Fig. 6.

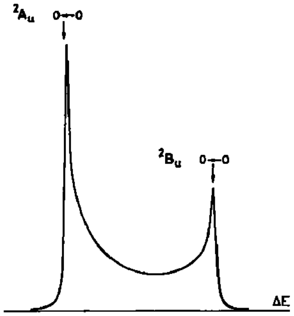


Fig. 6. *Calculated* Franck-Condon *envelope for the first two bands of* **7**. The barrier to internal rotation in the closed shell ground state of **7** was assumed to be 35 cm^{-1} (see text for details)

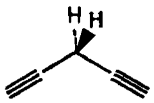
Two important conclusions can be drawn:

(1) The *Franck-Condon* envelope shows two prominent peaks situated within the limits of error at the two positions marked by the arrows ^2A_u and ^2B_u, which corresponds to the $0 \leftarrow 0$ transitions that would be due to the ejection of an electron from the anti-planar configurated molecule **7**. Thus the assumption of (almost) free internal rotation does not invalidate the analysis of the photoelectron spectrum in terms of a planar, rigid system.

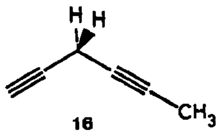
(2) The first peak slopes towards higher, the second towards lower ionization energies. This is indeed what is observed for the bands ① and ② of **7**. Consequently the recorded spectrum is in agreement with the assumption of (almost) free rotation of the two vinyl groups.

It should be noted that our analysis does not take into account the vibrational degrees of freedom of the molecule which tend to broaden the *Franck-Condon* envelope shown in Fig. 6. This broadening may be strong enough to almost obliterate the characteristic shape of this feature, as shown by the two strongly overlapping bands ③ and ④ in the spectrum of **7**.

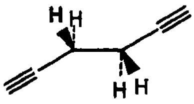
In Fig. 7 are shown the photoelectron spectra of diethynylmethane (**15** = 1,4-pentadiyne), 1,4-hexadiyne (**16**) and of 1,2-diethynyl-ethane (**17** = 1,5-hexadiyne) [22]. The characteristic data are collected in Table 4, and the results of SPINDO calculations for **15** and **17** in Tables 5 and 3 respectively.



15



16



17

From Fig. 7 it is immediately apparent that in all three cases an unequivocal assignment of the four π-bands ① to ④, which occur in the range of 9 to 12 eV, is rendered difficult by their strong overlapping.

In the spectra of **15** and **16** one observes two features at 10.3 and 11.0 eV or 9.8 and 10.6 eV, respectively, the intensity ratio of which is approximately 1:1. It is safe

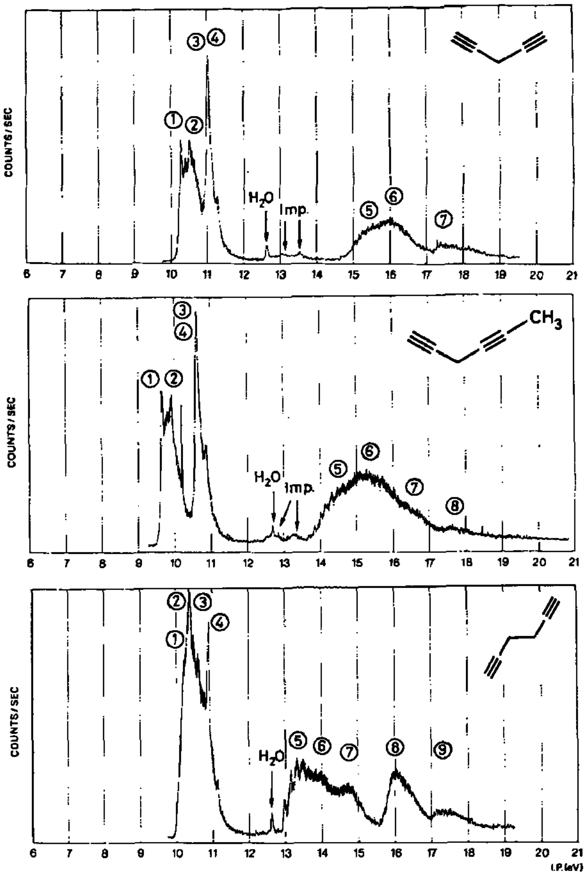


Fig. 7. *He(1)-photoelectron spectra of compounds* **15**, **16** *and* **17**

to assume that each feature corresponds to two strongly overlapping π-bands, *i.e.* bands ①, ② in the first, bands ③, ④ in the second. One of the π-bands in the second feature (presumably band ④) is dominated by a strong $0 \leftarrow 0$ vibrational component, which indicates that this band corresponds to the ejection of an electron from an almost pure π-orbital. On the other hand, the other component of the second feature (presumably band ③) seems to be rather broad, having its onset presumably in the region of the first feature. Such a band is usually associated with a strongly mixed orbital. The first feature is clearly composed of two π-bands ①, ② the shape of which leads us to expect that they have to be correlated with π-dominated orbitals which, however, should contain some σ-admixture.

From a purely qualitative point of view, the four π-orbitals of **15** which one might associate with bands ① to ④ are expected to be of the following type:

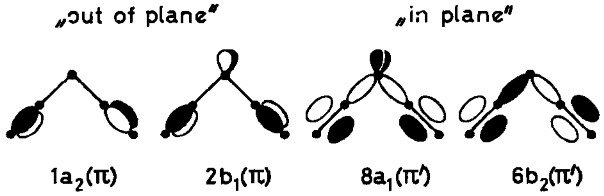
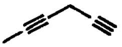
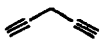


Table 4. *Experimental adiabatic* ($I_{a,j}$) *and vertical* ($I_{v,j}$) *ionization energies and spacing* $\tilde{\nu}$ *of the dominant vibrational fine structure of compounds* **15** *to* **17**.

Band	I_a (eV)	I_v [a)] (eV)	$\tilde{\nu}$, Remarks (cm^{-1})	Assignment	Band	I_a (eV)	I_v [a)] (eV)	$\tilde{\nu}$, Remarks (cm^{-1})	Assignment
15 $\{C_{2v}\}$ 					16 $\{C_s\}$ (assumed) 				
①	10.1_5	10.27	810	$2b_1(\pi)$	①	9.0	9.66	1210	$4a''(\pi)$
②		10.50	1860	$6b_2(\pi')$	②		9.91		$17a'(\pi')$
③, ④		11.02		$8a_1(\pi')$; $1a_2(\pi)$	③, ④		10.61	1850	$16a'(\pi')$; $3a''(\pi)$
⑤	14.70	15.5_0	shoulder	$7a_1$; $1b_1$;	⑤	13.78	14.55	1210	(σ)
⑥		16.0_0		$5b_2$; $6a_1$	⑥		15.2_0		
⑦		17.4		$4b_2$	⑦		16.6_0	shoulder	
⑧		18.0		$5a_1$	⑧		17.5		
⑨		22.6		$3b_2$	⑨		21.5		
17 $\{C_{2h}\}$ (assumed) 									
①	9.9_0	10.2_5		$9a_g(\pi')$					
②		10.37		$2a_u(\pi)$					
③		10.6_0		$2b_g(\pi)$					
④	10.88	10.88	1860	$8b_u(\pi')$					
⑤	12.98	13.31	1330	$1b_g$					
⑥		14.0		$8a_g$					
⑦		14.7_5		$7a_g$					
⑧	15.6_5	16.0_5		$7b_u$; $1a_u$					
⑨		17.4		$6a_g$; $6b_u$					

a) The PE.-spectra have been calibrated *in situ* with Ar, Xe and benzene (HeIα and β lines). Where two full decimals are given the ionization energies are correct to ± 0.02 eV; the vibrational spacings may be in error by ± 80 cm^{-1}.

Table 5. *Calculated orbital energies* ε_j *for compounds* **15**, **18** *and* **19** *according to the* SPINDO *method*

Orb.	$-\varepsilon$ (eV)	Description	Orb.	$-\varepsilon$ (eV)	Description	Orb.	$-\varepsilon$ (eV)	Description
15 $\{C_{2v}\}$ 			18 $\{C_s\}$ 			19 $\{C_2\}$ 		
$2b_1$	10.18	π_+ (87 % π)	14a'	9.83	58 % π_t, 4 % π_b	13a	9.84	56 % π_t, 9 % π_b
$6b_2$	10.33	π'_+ (95 % π')	10a''	9.98	29 % π_t, 44 % π_b	11b	10.03	25 % π_t, 47 % π_b
$8a_1$	10.57	π'_- (92 % π')	9a''	10.43	56 % π_t, 44 % π_b	12a	10.54	12 % π_t, 83 % π_b
$1a_2$	10.61	π_- (100 % π)	13a'	10.49	10 % π_t, 85 % π_b	10b	10.59	60 % π_t, 37 % π_b
$7a_1$	14.98		8a''	12.05	σ-Walsh	9b	12.04	σ-Walsh
$1b_1$	15.06	π (CH_2) 87 %	12a'	12.28	σ-Walsh	11a	12.24	σ-Walsh
$5b_2$	15.21		11a'	13.22	π-Walsh	8b	13.28	π-Walsh
$6a_1$	16.42		7a''	13.83	π-Walsh	10a	13.75	π-Walsh
$4b_2$	16.86		10a'	15.63		9a	15.66	σ-Walsh
$5a_1$	22.18		9a'	16.25		7b	16.09	
$3b_2$	23.23		6a''	16.28		8a	16.67	
$4a_1$	24.49		8a'	17.40	π-Walsh	6b	17.32	π-Walsh

'Through-space' interaction between the out-of-plane π-orbitals $1a_2(\pi)$, $2b_1(\pi)$ is expected to be smaller than between the two in-plane orbitals $8a_1(\pi')$, $6b_2(\pi')$, leading to the sequence $6b_2(\pi')$, $1a_2(\pi)$, $2b_1(\pi)$, $8a_1(\pi')$ in order of decreasing energy if only the 'through-space' interaction were operative. However, the 'through-space' induced splittings will be rather small and the orbital sequence therefore mainly dependent on 'through-bond' type interaction. Because of symmetry, $1a_2(\pi)$ is the pure linear combination of the two out-of-plane basis π-orbitals and must therefore be associated with the sharp band at $I_{v,4} = 11.0$ eV in the spectrum of **15**. All other linear combinations can mix with σ-orbitals of appropriate symmetry, namely the $b_1(\pi)$ combination with the methylene pseudo-π orbital, yielding $2b_1(\pi)$, and the $a_1(\pi')$ and $b_2(\pi')$

linear combinations with all the other σ-orbitals belonging to the irreducible representations A_1 or B_2. It is of course rather difficult to assess the corresponding through-bond shifts of the orbital energies, but the results of a SPINDO calculation presented in Table 5 and in Fig. 8 suggest the qualitative picture for the rationalization of the observed spectra of **15** and of **16** shown in Fig. 9.

The positive displacements of 0.4 to 0.6 eV of the orbital energies, going from **15** to **16** are due to the inductive and/or hyperconjugative influence of the methyl group.

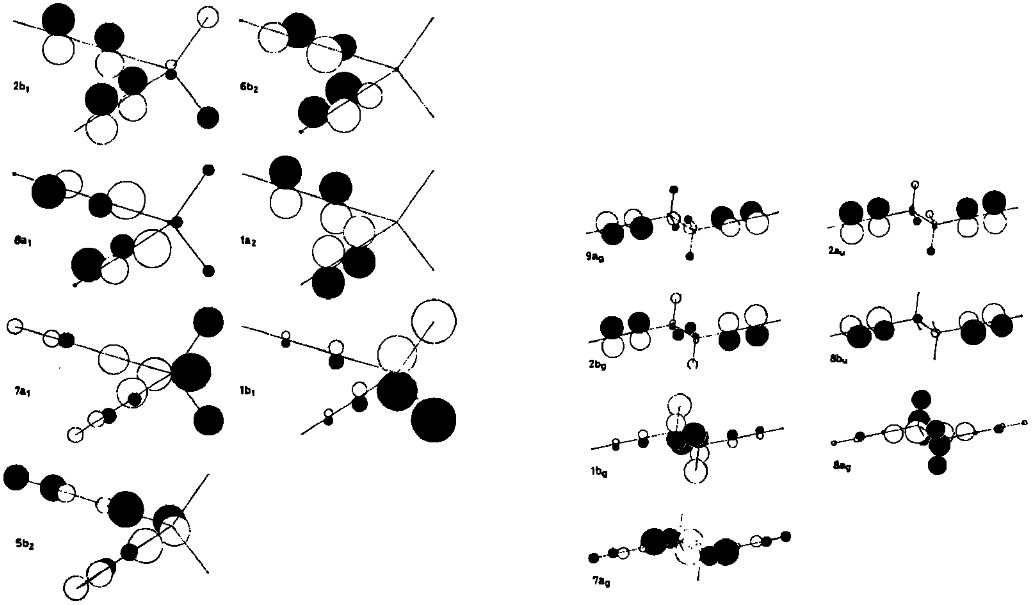


Fig. 8. *Molecular orbitals* (SPINDO) *of* **15** *and* **17**. (Same order as in Fig. 4)

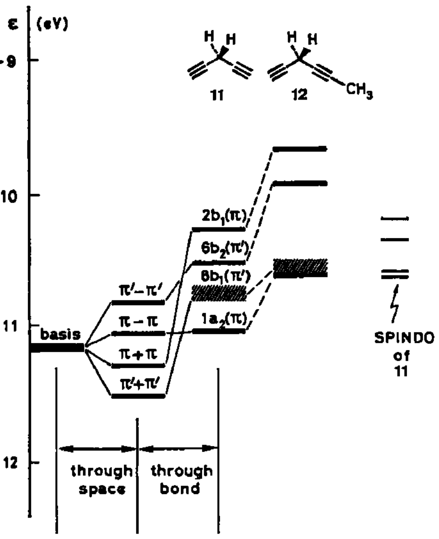


Fig. 9. *Molecular orbital diagram for* **15**, *demonstrating the effect of 'through-space' and 'through-bond' interaction*

In addition the reduction of the symmetry from C_{2v} in **15** to C_s (at best) in **16** leads to additional mixing of orbitals belonging to the irreducible representations A_2 and B_1 or to A_1 and B_2 in **15**.

The analysis of the spectrum of 1,5-hexadiyne (**17**) is even more complicated because the first three bands ①, ②, ③ overlap completely, leading to the non resolvable feature at 10.4 eV. In addition the question arises whether we have to assume that this molecule is present in the gas phase in a single preferred conformation, *i.e.* the one in which the two acetylenic groups are anti-planar, or as a mixture of anti-planar and gauche conformers. *Bischof et al.* [22], who have analysed the photoelectron spectrum of **17**, calculated that the anti-planar conformation is preferred over the gauche conformation by 40 kJ mol^{-1}. Consequently they have interpreted the spectrum of **17** in terms of this conformation only.

Dewar's MINDO/3 model [21], which has been shown to reproduce the enthalpies of formation of a large variety of hydrocarbons with excellent agreement [23], yields for the internal rotation of **17** the potential shown in Fig. 10, if standard-geometry parameters are used [24]. It is seen that the energy difference between the syn- and the anti-planar conformations amounts to 42.6 kJ mol^{-1}, in excellent agreement with the value quoted in [22]. The most noteworthy result is, that the gauche conformations do not correspond to a local minimum on the potential curve. However, because of the rather shallow minimum at 180° one expects that all the antiperiplanar conformations of **17** contribute significantly to its photoelectron spectrum.

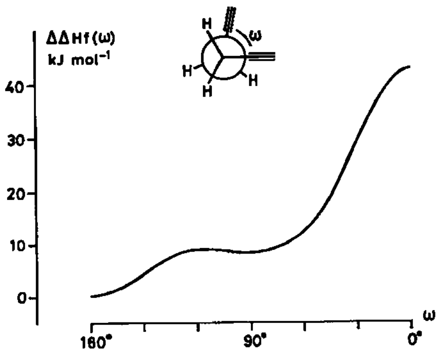
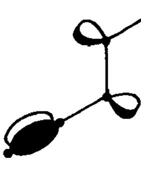
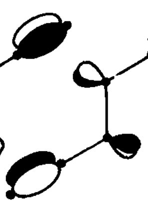
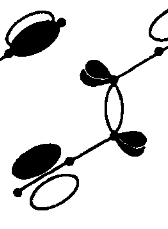


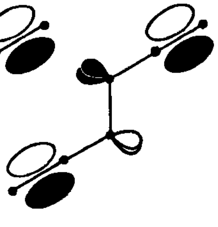
Fig. 10. *Potential* $V(\omega)$ *for internal rotation in ground state* **17**. Results according to the MINDO/3 method using standard geometry

Qualitatively the four orbitals of predominant π-character of anti-planar **17** can be visualized as follows:


$2a_u(\pi)$


$2b_g(\pi)$


$9a_g(\pi')$

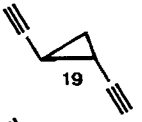

$8b_u(\pi')$

From these diagrams it is obvious that the relative sequence of the orbitals is completely determined by through-bond interactions. If this is so, then we would expect that $8b_u(\pi')$ exhibits the least destabilization relative to the π-orbital basis energy A_t, because the orbital with which the linear combination $(\pi'_t - \pi'_{t'})/\sqrt{2}$ can interact is the rather low lying combination of the four CH-σ-orbitals, belonging to B_u. Therefore the rather sharp band ④ at 10.9 eV has to be associated with the ejection of an electron from this particular orbital, as has been proposed by *Bischof et al.* [22].

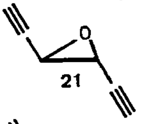
To support their assignment, we have carried out SPINDO calculations for **17**, which are summarized in Table 3 and in Fig. 5 and 8. From Fig. 5, which shows the dependence of the orbital energies on the twist angle ($\omega = 0$: syn-planar; $\omega = \pi$: anti-planar), it is obvious that the characteristic shape of the feature resulting from the three overlapping bands ①, ②, ③ with band ④ set apart is only compatible with the assumption that the anti-planar conformer dominates. Major admixture of the other conformers would lead to an unresolvable merger of all four bands. Finally, the orbital diagrams given in Fig. 8 are in agreement with the qualitative arguments presented above.

To conclude we shall now discuss the photoelectron spectra of *cis*- and *trans*-diethynylcyclopropane (**18**, **19**), *cis*- and *trans*-diethynyl ethylene oxide (**20**, **21**) and of *cis*- and *trans*-diethynyl ethylene sulfide (**22**, **23**) which are shown in Fig. 11, 12, 13 and in Table 6.


18


19


20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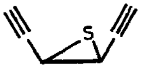
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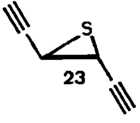

23

The hydrocarbons **18** and **19** differ from **8** and **9** in their orbital build-up in that the *Walsh*-orbitals e'_S, e'_A of the cyclopropane moiety have now taken the place of the ethylenic π-orbital π_d. In view of the known conjugating abilities of the *Walsh* orbitals, one might have expected that the two sets of photoelectron spectra *i.e.* those of **8**, **9** and of **18**, **19** are closely related, as has previously been observed in similar cases [25]. However, this is not quite the case, although the general features at lower ionization energies do exhibit some common characteristics.

The highest occupied orbitals of cyclopropane are, according to its photoelectron spectrum [26] and using *Koopmans'* approximation 3e' (−10 to −12 eV), 1e'' (−13 eV), $3a'_1$, $1a''_2$ (−15 to −17 eV) the relative sequence of the last two orbitals being uncertain [27]. The first band shows a large *Jahn-Teller* split, as expected for the removal of an electron from a degenerate orbital *e.g.* 3e' [28]. The real representations of the 3e' *Walsh* orbitals are:

(24)

D_{3h}	c'_S	e'_A
C_s	a'	a''
C_2	a	b

Of these, e'_S, which is symmetric with respect to σ of C_s and $C_2(z)$ of C_2, plays the role of the π-orbital π_d of the ethylenic bond in **8** and **9**, whereas e'_A corresponds in its symmetry behaviour to π^*, the antibonding π-orbital. However, being a bonding orbital, it mixes effectively with the other orbitals of same symmetry. This is the main reason for the major discrepancies between the spectra of **8**, **9** and **18**, **19**.

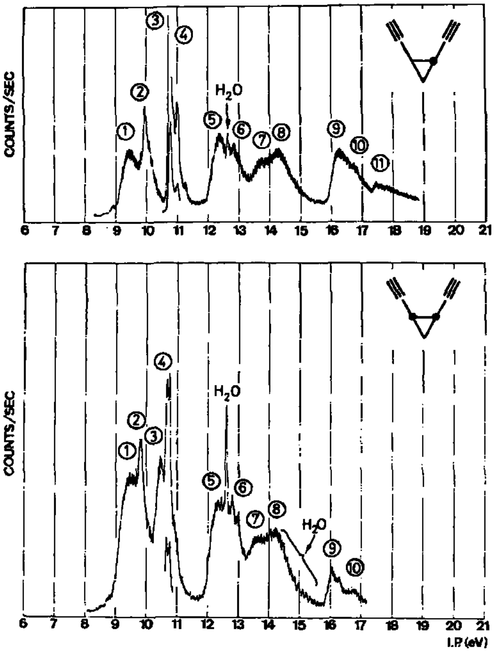


Fig. 11. *He(I)-photoelectron spectra of compounds* **18** *and* **19**

In addition to this, there is another complicating feature which renders a straightforward qualitative analysis difficult: there is no unique way for choosing the orientation of the π-orbitals of the acetylenic moieties in **18** and **19**. An obvious choice seems to be the one in which two of the π-orbitals are parallel to the two p-components of c'_S (see (24)) and are thus 'tangential' to the three-membered ring ($\pi_t, \pi_{t'}$), whereas the other, orthogonal pair points along the bisectrix of the corresponding CCC-angle $\pi_b, \pi_{b'}$). However, these orbitals tend to mix considerably, *i.e.* they will appear to have rotated by large angles around their C≡C-axes in the different molecular orbitals.

For these reasons it is preferable to rely on a semi-empirical model, *e.g.* the SPINDO-treatment. The results for **18** and **19** are summarized in Table 5 and in the orbital diagrams of Fig. 14, which are self-explanatory.

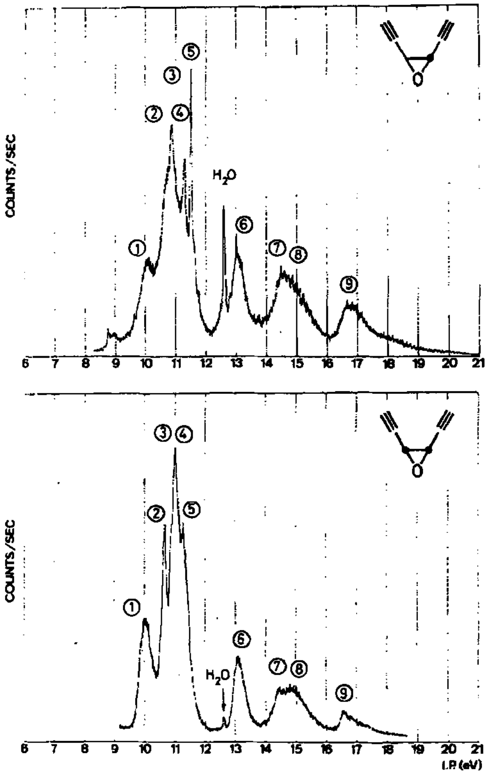


Fig. 12. *He(I)-photoelectron spectra of compounds* **20** *and* **21**

In agreement with expectation, the four highest occupied orbitals are those which are dominantly π in character. Both in **18** and in **19** they are predicted to form two groups of two orbitals each, in complete correspondence with what is observed in the spectra of Fig. 11 where the bands labelled ①, ② and ③, ④ overlap by pairs in two well separated regions at 9 to 10 eV and 10.5 to 11 eV. Furthermore, the change in configuration from *cis* to *trans* is predicted to have only little influence on the π-band positions except for an interchange of the orbitals correlated with the second group of bands ③, ④ at 10.5 to 11 eV, in as far as their linear combinations in terms of π_t and π_b are concerned: Whereas the third orbital 9a″ of **18** is calculated to be a one-to-one mixture of these two types of basis orbitals and the fourth 13a′ almost pure π_b, the reverse is found for the two orbitals 12a and 10b of **19**. It is gratifying but perhaps not significant that this reversal seems indicated in the photoelectron spectra of **18** and **19**. In **18** the broader of the two bands ③, ④ preceeds the sharper one, whereas the reverse is suggested by the spectrum of **19**. Furthermore the theoretical calculation suggests that only the two top occupied orbitals 14a′, 10a″ of **18** and 13a, 11b of **19** are strongly mixed with the *Walsh* orbitals. This explains why the corresponding bands are wider than those of the second group. The close agreement between the calculated and 'observed' orbital scheme suggests, that the correlation diagram shown in Fig. 15 constitutes presumably a reasonable assignment which can be used as a basis for a rationalization of the photoelectron spectra of the remaining four compounds **20** to **23**, shown in Fig. 12 und 13.

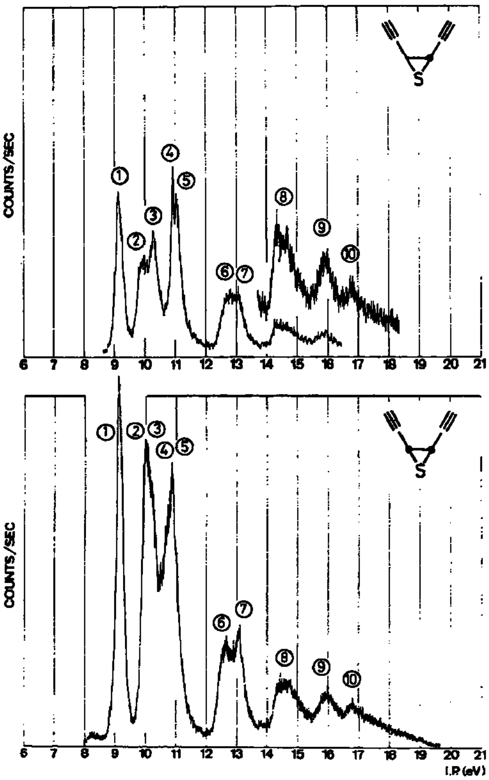


Fig. 13. *He(I)-photoelectron spectra of compounds* **22** *and* **23**

Table 6. *Experimental adiabatic* ($I_{a,j}$) *and vertical* ($I_{v,j}$) *ionization energies and spacing* $\tilde{\nu}$ *of the dominant vibrational fine structure of compounds* **18** *to* **23**.

Band	I_a	I_v [a]	Assignment
	(eV)		
18 $\{C_s\}$			
①	8.90	9.50	14a'(π)
②		9.82	10a''(π)
③		10.47	9a''(π)
④		10.77	13a'(π)
⑤	11.80	12.35	8a'' (σ-Walsh)
⑥		12.8	12a' (σ-Walsh)
⑦		13.6_5	11a' (π-Walsh)
⑧		14.20	7a'' (π-Walsh)
19 $\{C_2\}$			
①	9.00	9.40	13a(π)
②		9.93	11b(π)
③, ④	10.78	10.78 [b]	12a(π); 10b(π)
⑤	11.9_5	12.3_5	9b (σ-Walsh)
⑥		12.8_0	11a (σ-Walsh)
⑦		13.70	8b (π-Walsh)
⑧		14.2_5	10a (π-Walsh)

Band	I_a	I_v [a]	Assignment
	(eV)		
20 $\{C_s\}$			
①	9.6_0	10.0_5	14a'(n)
②		10.68	13a'(π); 12a'(π); 10a''(π); 9a''(π)
③, ④		11.03	
⑤		11.30	
⑥	12.8_0	13.0_5	11a' (σ-Walsh)
⑦	14.0	14.5_5	8a'' (σ-Walsh)
⑧		14.9_0	7a'' (π-Walsh)
⑨		16.8_0	10a' (σ-Walsh)
21 $\{C_2\}$			
①	9.5_0	10.07 [c]	11b(n)
②, ③		10.82	10b(π); 9b(π) 13a(π); 12a(π)
④		11.29	
⑤		11.51	
⑥	12.6_5	13.0_5	11a (σ-Walsh)
⑦	14.0	14.5_0	8b (σ-Walsh)
⑧		15.0	10a (π-Walsh)
⑨	16.2	16.7_5	9a (σ-Walsh)

Band	I_a	I_v [a]	Assignment
	(eV)		
22 $\{C_s\}$			
①	8.8_0	9.14	17a'(n)
②, ③	9.7_0	10.0_0	16a'(π); 15a'(π) 11a''(π); 10a''(π)
④, ⑤		10.88	
⑥		12.6_5	9a'' (σ-Walsh)
⑦		13.1_0	14a' (σ-Walsh)
⑧		14.5_5	8a'' (π-Walsh)
⑨		15.9_5	13a' (σ-Walsh)
⑩		16.6_5	12a' (π-Walsh)
23 $\{C_2\}$			
①	8.8_5	9.14	13b(n)
②	9.6_0	9.90	12b(π); 11b(π); 15a(π); 14a(π)
③		10.38	
④		10.92	
⑤		11.05	
⑥		12.6_5	10b (σ-Walsh)
⑦		13.0_0	13a (σ-Walsh)
⑧		14.4_5	12a (π-Walsh)

a) The PE.-spectra have been calibrated *in situ* with Ar, Xe and benzene (HeIα and β lines). Where two full decimals are given the ionization energies are correct to ± 0.02 eV; the vibrational spacings may be in error by ± 80 cm^{-1}.

b) $\tilde{\nu}$ = 2000 cm^{-1}.

c) The peaks at 8.8 and 9.0 eV are due to the Heβ line.

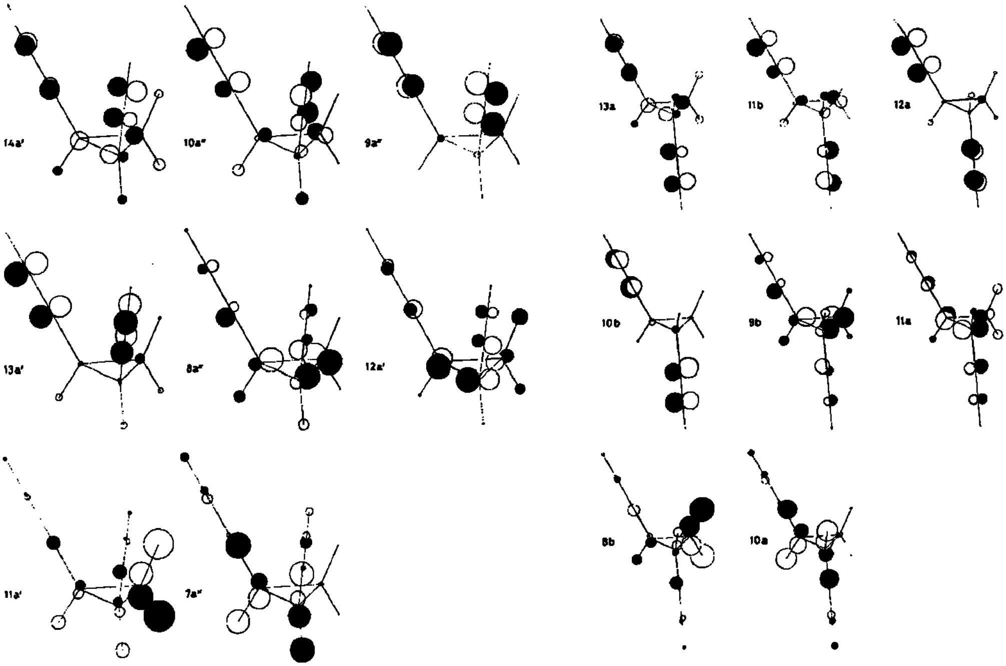


Fig. 14. *Molecular orbitals* (SPINDO) *of compounds* **18** *and* **19** (Same order as in Fig. 4)

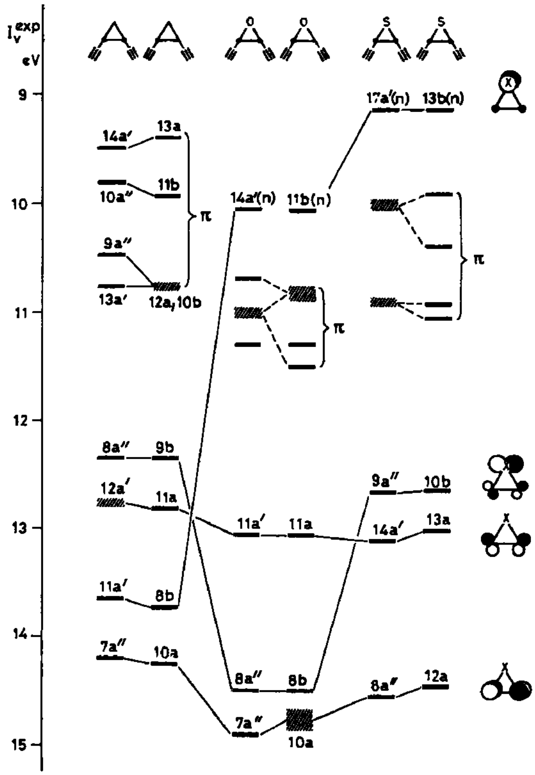
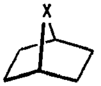


Fig. 15. *Correlation diagram and assignment of the bands in the photoelectron spectra of compounds* **18** *to* **23**

Apart from those shifts resulting from the replacement of the methylene group in **18** and **19** by an oxygen or sulfur centre, we expect additional bands in the photoelectron spectra of **20** to **23** which stem from the ejection of an electron from the lone-pair orbitals of the oxygen or sulfur atom. The corresponding bands in the photoelectron spectra of the systems **24** to **29** have been observed at the following positions ($I_{v,1}$ in eV):

	HXH	MeXH	MeXMe	iPrXiPr		
	24	**25**	**26**	**27**	**28**	**29**
X = O	12.62 [4]	10.96 [30]	9.94 [26]	9.2 [26]	9.57 [26]	10.57 [33,34]
X = S	10.46 [4]	9.42 [31,32]	8.65 [31,32]	8.26 [31,32]	8.43 [26]	9.00 [34,35]

(25)

These values leave no doubt that the bands ① (at 10.0_5 eV and 9.1_5 eV in the spectra of **20**, **21** and **22**, **23** respectively) are lone-pair bands. This is shown in the correlation diagram of Fig. 15. The remaining bands in the region 10 to 12 eV for **20**, **21** and 9.5 to 11.5 for **22**, **23** should be closely related to those of the hydrocarbons **18**, **19**, these orbitals being centred mainly on the acetylenic moieties. However, it does not seem possible to deduce an assignment. On the other hand, the bands observed in the region $I_{v,j} > 12$ eV seem to follow the pattern expected from previous experience. Nevertheless, the correlation indicated in Fig. 15 must be considered as tentative, at best.

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