

170. The Ionization Energies of Di-*n*-Alkyl Diacetylenes

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Summary

The He(I α) photoelectron spectra and the ionization energies of symmetrically substituted di-*n*-alkyl-diacetylenes R-(C \equiv C)₂-R (with R = CH₃, C₂H₅, *n*-C₃H₇, *n*-C₄H₉) are presented. The effect of the alkyl substituents is that the two acetylenic ionization energies, $I_{v,1}$ and $I_{v,2}$, shift by the same amount, *i.e.* their difference $I_{v,2} - I_{v,1}$ remains constant (2.45 ± 0.05 eV). Between 12.5 eV and 17 eV the band system in the photoelectron spectrum of R-(C \equiv C)₂-R is superimposable with that in the spectrum of the corresponding alkane, RH, with the exception of a uniformly small shift of all the bands to higher ionization energy.

The influence of the replacement of one or both hydrogen atoms H by (an) alkyl group(s) R on the ionization energies $I_{v,j}(\pi)$ of acetylene and polyacetylenes H-(C \equiv C)_{*n*}-H has first been studied, for the special case R = Methyl, by Turner & Baker [1] and later by our group [2]. However, the most comprehensive and careful study in this field is that of Mouvier *et al.* [3] who investigated 11 monosubstituted and 25 disubstituted acetylenes with 16 different kinds of alkyl groups R in various combinations. In this note we complement their results by examining the ionization energies $I_j(\pi)$ and $I_j(\sigma)$ of the symmetrically substituted dialkyl acetylenes (*n* = 2) with R = methyl, ethyl, *n*-propyl and *n*-butyl.

The photoelectron spectra of these four hydrocarbons, recorded with He(I α) radiation with a resolution of $E/\Delta E \approx 200$ are shown in Fig. 1.

The first two bands at 10.17 eV and 12.62 eV in the photoelectron spectrum of the parent compound diacetylene (R = H) correspond to the $\tilde{X}^2\Pi_g$ and $\tilde{A}^2\Pi_u$ states of the radical cation [1], *i.e.* states generated by the ejection of an electron from one or the other of the two π -orbital pairs of the parent hydrocarbon.

This has been established unambiguously by correlation with the spectra of homologous acetylenes (*n* = 1, 3, 4) [2] [4] and of halo- or dihalo-diacetylenes [5]. Although the dialkyl-acetylenes with R = Et, *n*Pr, *n*Bu lack a higher order axis, we shall keep the above state labels for the sake of convenience. The relevant data have been collected in Tab. 1. The ionization energies given correspond to the position of the 0 \leftarrow 0 vibrational component in the bands and are thus close enough to the vertical ones for all practical purposes. Due to the (partial) overlap with the σ -bands of the alkyl moieties the value of the vertical ionization potentials of the second bands in the spectra of di-*n*-propyl- and di-*n*-butyl-diacetylene are somewhat uncertain.

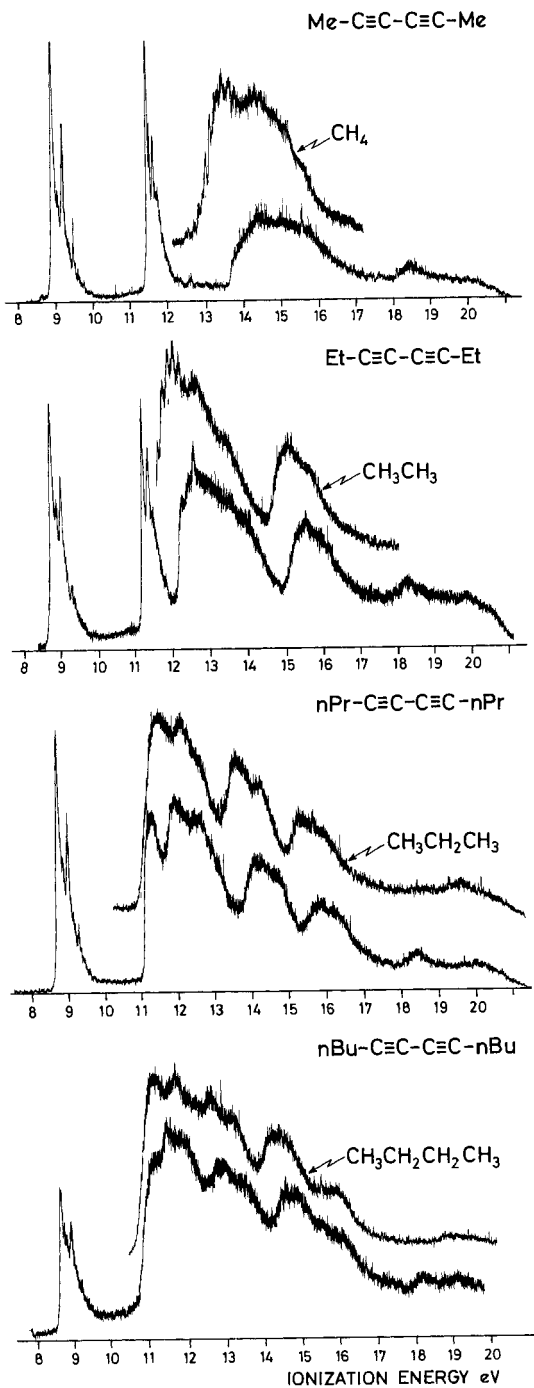


Fig. 1. *He(I α) excited photoelectron spectra of dialkyl diacetylenes, $\text{R}-(\text{C}\equiv\text{C})_2-\text{R}$, and those of the corresponding alkanes, RH*

Comments. – 1) As expected the shifts of the two π -bands under the influence of alkyl substitution are in essential agreement with the ones observed by *Mouvier et al.* for the mono substituted acetylenes R–C \equiv CH: R = Methyl (–1.04 eV), Ethyl (–1.23 eV), *n*-Propyl (–1.31 eV), *n*-Butyl (–1.23 eV) [3]. It is noteworthy that within the limits of error both bands shift by the same amount, with perhaps a slight indication that the shift of the second band is marginally smaller (*e.g.* –1.14 eV *vs.* –1.25 eV in the spectrum of dimethyl diacetylene). This result is perhaps not what one might have expected on the basis of a rule proposed by *Houk et al.* [6], which says that the alkyl group induced shifts should increase with increasing ionization energies, i.e. that they should be larger for the second band than for the first in our spectra (see also *Fig. 13* of [7]).

2) As a consequence of the above observation, the split $\Delta = I(\tilde{A}^2\Pi_u) - I(\tilde{X}^2\Pi_g)$ is unaffected by the two alkyl substituents R, within approximately ± 0.05 eV. This is supported by the much more precise values derived from the radical cation emission spectra of R–(C \equiv C) $_2$ –R $^+$ [8] which yield: R = H (2.445 \pm 0.001 eV); Methyl (2.549 \pm 0.002 eV); Ethyl (2.488 \pm 0.002 eV). It should be mentioned that the interaction matrix element between two conjugated triple-bond π -orbitals has been found to be $B = \langle \pi | \mathcal{H} | \pi \rangle = -1.225$ eV from an analysis of mono- and disubstituted diacetylenes [2], using an equivalent orbital model. The ‘predicted’ split $\Delta = 2|B| = 2.45$ eV is in excellent agreement with the observed ones given in *Tab. 1*.

Table 1. Ionization Energies of Dialkyldiacetylenes, corresponding to the $\tilde{X}^2\Pi_g \leftarrow X^1\Sigma_g^+$ and $\tilde{A}^2\Pi_u \leftarrow X^1\Sigma_g^+$ transition (all values in eV)

R	Radical Cation State		Shifts relative to R = H		Split ^{a)} Δ
	$\tilde{X}^2\Pi_g$	$\tilde{A}^2\Pi_u$	$\tilde{X}^2\Pi_g$	$\tilde{A}^2\Pi_u$	
H ^{b)}	10.17	12.62	–	–	2.45
CH ₃	8.92	11.48	–1.25	–1.14	2.56
C ₂ H ₅	8.78	11.25	–1.39	–1.37	2.47
<i>n</i> -C ₃ H ₇	8.72	11.2 ^{b)}	–1.45	–1.4 ₂	2.4 ₈
<i>n</i> -C ₄ H ₉	8.67	11.1 ^{c)}	–1.50	–1.5 ₂	2.4 ₃

a) Split $\Delta = I(\tilde{A}^2\Pi_u) - I(\tilde{X}^2\Pi_g)$.

b) Uncertain to ± 0.05 eV.

c) Because of partial overlap with the first σ -band, uncertain by ~ 0.05 to 0.1 eV.

3) The photoelectron spectrum of diacetylene has a window from ~ 12.5 eV to ~ 17 eV, because the first σ -band ($\tilde{B}^2\Sigma_g^+$ state of the radical cation) is located at 17.5 eV [1]. The corresponding bands in the spectra of the dialkyl-diacetylenes are apparently above 17 eV. Therefore, the σ -band-system due to the alkyl groups R in the spectra shown in *Fig. 1* are uncontaminated by other bands due to ionization processes not ‘located’ in these groups. On top of the individual spectra of the compounds R–(C \equiv C) $_2$ –R we have superimposed the spectra of the respective alkanes RH recorded on the same spectrometer and under comparable conditions. Disregarding the intensity changes due to the differing experimental conditions, they agree completely with those recorded by *Price, Potts & Streets* [9].

It is a remarkable fact that the envelopes of the σ -band-systems in the photoelectron spectra of both the molecules R–(C \equiv C) $_2$ –R and RH are practically super-

Table 2. Comparison of σ -Type Ionization Energies of $R-C\equiv C-C\equiv C-R$ with those of the corresponding Hydrocarbons (all values ± 0.1 eV)

CH ₄	CH ₃ ^{a)}	Δ ^{b)}	C ₂ H ₆	C ₂ H ₅ ^{a)}	Δ ^{b)}	C ₃ H ₈	<i>n</i> -C ₃ H ₇ ^{a)}	Δ ^{b)}	<i>n</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₉ ^{a)}	Δ ^{b)}
13.6	14.3	0.7	12.1	12.7	0.6	11.5	12.0	0.5	11.2	11.5	0.3
14.4	15.1	0.7	12.7	13.4	0.7	12.1	12.6	0.5	11.7	12.0	0.3
15.0	15.7	0.7	13.3	14.0	0.7	12.6	–	–	11.7	(12.0)	(0.3)
			15.0	15.6	0.6	13.5	14.1	0.6	12.2	–	–
			15.8	(16.2) ^{c)}	(0.4) ^{c)}	14.1	14.7	0.6	12.7	12.9	0.2
						15.2	15.8	0.6	13.2	13.5	0.3
						16.0	(16.2) ^{c)}	(0.2) ^{c)}	14.3	14.6	0.3
									14.6	14.8	0.2
									16.0	(16.0) ^{c)}	(0.0) ^{c)}

a) Alkyl group R in $R-(C\equiv C)_2-R$.

b) Δ = Difference in ionization energy of σ -type band of dialkyl diacetylenes and corresponding band in the alkane.

c) Values given in parentheses are tentative.

impossible, except for a small shift which is constant for a given R independent of the ionization energy within the band system (see *Tab. 2*). Due to the uncertainties in the ionization energies of the broad bands of the alkanes and the dialkyl diacetylenes, it is difficult to determine the precise relationship that would describe the shifts in σ ionization energy as a function of R. There is, however, an indication that the shift of the σ -band system decreases with increasing size of the group R.

From this observation one deduces that the alkane orbitals carry over rather well to the alkyl groups in the diacetylenes $R-(C\equiv C)_2-R$ and that the hyperconjugative interaction with the triple bond π -orbitals is about the same for all of them.

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