191. Electronic States of Di-*t*-butylpolyacetylene Radical Cations

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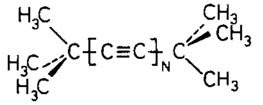
Summary

The π-ionization energies of the di-*t*-butylpolyacetylenes with two, three, four and five conjugated triple bonds have been determined by He(Iα) photoelectron spectroscopy. The assignment of the bands to the Π-states of the corresponding radical cations follows from simple correlations in agreement with previous experience. The influence of the *t*-butyl groups on the ionization energies is rationalized in terms of traditional, qualitative arguments assuming an inductive and/or hyperconjugative mechanism. However, a more careful analysis shows that the 'The-higher-the-ionization-energy-the-higher-the-alkyl-induced-shift' rule is not always true.

The classical work of *Bohlmann* [1] demonstrated that the stability of polyacetylenes could be magnified considerably by the introduction of alkyl groups at the terminal positions, particularly if the alkyl groups are *t*-butyl groups. Therefore these molecules are ideal substrates to study the effects of triple bond homologation on the energies of their radical cationic states as a function of the number of triple bonds.

In *Figure 1* are shown the He(Iα) photoelectron spectra of the di-*t*-butylpolyacetylenes $C_{2N+8}H_{18}$ with N = 2, 3, 4 and 5 triple bonds, the case N = 1 having



1 (N)

been studied by *Mouvier et al.* [2]. Free rotation of the *t*-butyl groups requires the conformations of these molecules to belong to the symmetry groups D_3, D_{3d}, or D_{3h}, depending on the instantaneous twist angle. However, in the following discussion we shall classify states and orbitals with respect to an idealized $D_{\infty h}$ symmetry.

Of the 4N + 25 occupied valence shell molecular orbitals of **1**(N) 2N + 9 are σ-orbitals and 2N + 16 π-orbitals, 16 of which are localized mainly in the two *t*-butyl groups and 2N in the polyacetylene moiety. Thus, in accordance with previous experience deduced from the work of *Turner & Baker* [3] and our own [4], we expect N sharp bands corresponding to $^2\Pi$-states of the radical cation $\mathbf{1}^+$(N)

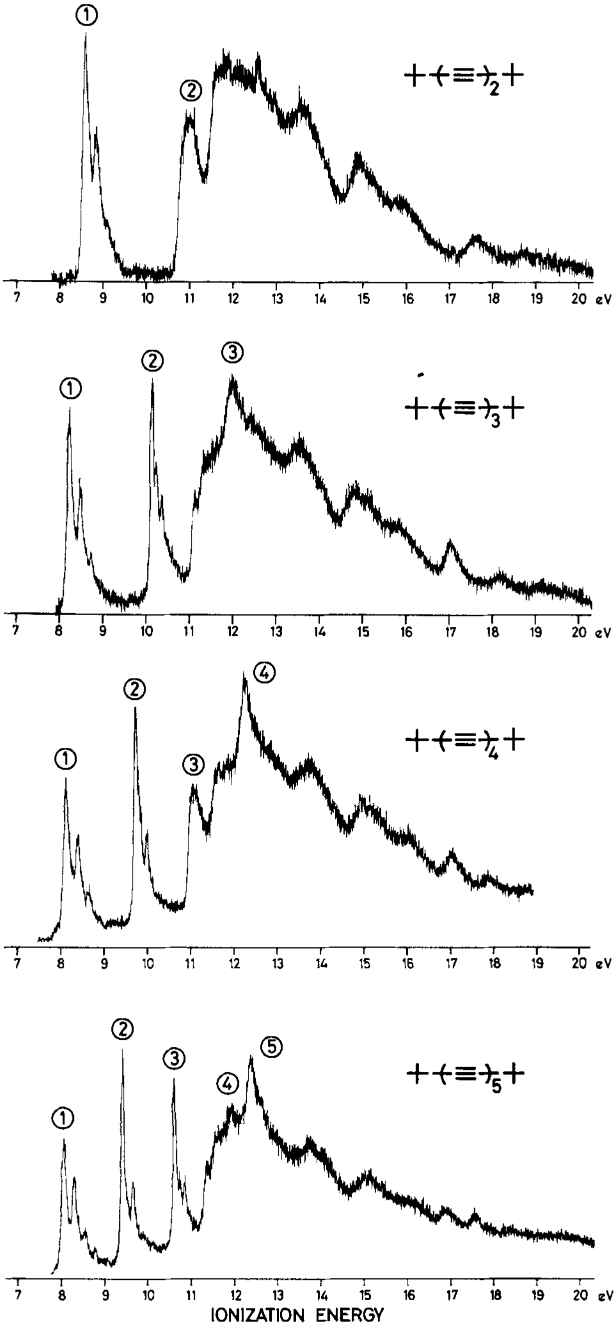


Fig. 1. *He(Iα) photoelectron spectra of the di-*t*-butylpolyacetylenes* t-*Bu-(C≡C)*$_N$-t-*Bu with* $N = 2, 3, 4$ *and 5.* The N numbered band maxima refer to those $^2\Pi$-states which are due to electron ejection from a polyacetylene type π-orbital

due to the removal of an electron from one of these N pairs of degenerate orbitals. As can be seen from *Figure 1* the π-bands at higher energy (above ~11.5 eV) are obscured by the complex band system due to the removal of an electron from one of the *t*-butyl group orbitals. However, in a recent contribution we have shown [5] that the band system due to the alkyl groups R in the photoelectron spectra of dialkyldiacetylenes $R-(C\equiv C)_2-R$ is superimposable (except for a minor shift of the band system as a whole) with that of the corresponding hydrocarbon RH. It is therefore possible, by subtracting the slightly shifted photoelectron spectrum of isobutane from the spectra of **1**(3), **1**(4) and **1**(5) presented in *Figure 1*, to locate with some confidence those missing π-bands which are associated with the ejection of an electron from π-orbitals which are best represented as linear combinations of acetylenic two centre π-orbitals. The corresponding maxima are labelled 1 to N in the photoelectron spectra of **1**(N) given in *Figure 1* and their positions are recorded in *Table 1* and in the correlation diagram shown in *Figure 2.* Note that the values given are the positions I_j^m of the band maxima, *i.e.* positions which are close, but not necessarily identical, to the ones corresponding to the vertical ionization energies I_j^v.

(1) The correlation diagram shown in *Figure 2* is self-explanatory. It closely resembles the one presented earlier for the series acetylene **2**(1) to tetraacetylene **2**(4) [4], except for the shifts induced by the *t*-butyl groups. The first bands are dominated by vibrational fine structure corresponding to the excitation of C≡C stretching modes. The excitation of these modes is also evident on the other π bands lying below 11 eV for N=3, 4 and 5. The σ/π onsets due to the two *t*-butyl groups can be seen to lie at ≈ 11 eV both in the spectrum of **1**(3) and **1**(5). Thus the corresponding onsets in the spectra of **1**(2) and **1**(4) also must lie at ≈ 11 eV and thus overlap with the π bands marked ② and ③ respectively. This causes the apparent loss in vibrational fine structure for these π bands. In addition, the loss of fine structure in such bands as ② of **1**(2) or ③ of **1**(4) could also be due in part to the conjugative mixing of the triple bond π-orbitals with the pseudo-π-orbitals of the *t*-butyl groups. When an electron vacates such a mixed orbital a large number of low frequency bending modes are activated in the radical cation.

Table 1. *Ionization energies* I_j^m (= Positions of band maxima) *of the first N π-bands in the photoelectron spectra of di-*t*-butylpolyacetylenes* **1**(N) (All values in eV. Estimated errors ±0.02 eV for values given with two decimals; ±0.05 eV if one decimal given)

Band[a]	State[b]		**1**(1)[c]	**1**(2)	**1**(3)	**1**(4)	**1**(5)
	N = odd	N = even					
①	$^2\Pi_u$	$^2\Pi_g$	9.05	8.61	8.32	8.12	8.06
②	$^2\Pi_g$	$^2\Pi_u$		11.06	10.27	9.78	9.44
③	$^2\Pi_u$	$^2\Pi_g$			12.0[d]	11.13	10.62
④	$^2\Pi_g$	$^2\Pi_u$				12.3[d]	11.8[d]
⑤	$^2\Pi_u$						12.4[d]
			Approximate value of σ-onset ≈ 11 eV				

[a] The band numbers refer to those given in *Figure 1.* [b] Labels refer to an idealized $D_{\infty h}$ symmetry. [c] Value taken from [2]. [d] Band overlapped by σ/π-band system due to the two *t*-butyl groups.

(2) The photoelectron spectra of the unsubstituted polyacetylenes **2**(N) could only be obtained for N = 1, 2 [1] and 3, 4 [2]. Pentaacetylene **2**(5) [6] was judged to be much too unstable to allow a gas-phase spectrum to be recorded. Therefore, the *t*-butyl group induced shifts can only be assessed for the first four members of the set **1**(N). In *Figure 3* are shown bar diagrams for the π-ionization energies of **2**(N) and **1**(N) (N = 1, 2, 3, 4) and the observed band shifts

$$\Delta(j) = I_j^m(\mathbf{2}(N)) - I_j^m(\mathbf{1}(N)) \tag{1}$$

The sum of the shifts and the mean band shifts $\bar{\Delta}$ depend on N as follows (in eV):

N	1	2	3	4
$\Sigma_j \Delta(j)$	2.35	3.12	3.30	3.69
$\bar{\Delta}$	2.35	1.56	1.10	0.92

(2)

This result needs a few comments. A naive *Hückel* perturbation treatment based on a linear combination of semi-localized two-centre π-orbitals, demands that the sum $\Sigma_j \Delta(j)$ be independent of N, if the perturbing influence of the *t*-butyl group is limited to the basis π-orbitals of the directly substituted triple bond. On the other hand, it has become customary in the traditional LFER-type treatments (LFER = linear free energy relationship [7]) to assume that the perturbation of the terminal bonds (*e.g.* an inductive destabilization δA of the π-orbital basis energy A) is transmitted from one bond to the next, the transmittance factor being $m \approx 1/3$. Under this assumption, the above sum should depend on N as follows:

$$\Sigma_j \Delta(j) = 2\delta A \left(\frac{1-m^N}{1-m}\right) \tag{3}$$

Applying (3) to the data listed in (2) yields by a least squares calculation $\delta A = 1.15$ eV and $m = 0.365$, *i.e.* a value not significantly different from $m \approx 1/3$. The residual error for the sums $\Sigma_j \Delta(j)$ is 0.14 eV. Thus, the results given in (2) conform to what one might have expected from the usual 'chemical' experience, *i.e.* that embodied in a LFER model. The value of δA compares well to that which can be derived from the data obtained by *Mouvier et al.* [2] or from the perturbations caused by *t*-butyl groups on the ionization energies of other unsaturated systems [8].

(3) *Figure 3* shows that for a given pair **1**(N), **2**(N), the shifts $\Delta(j)$ depend somewhat on j. If we assume the simplest model possible, *i.e.* a ZDO linear combination of triple bond π-orbitals, then the expected value of the individual shifts can be calculated by a trivial first order perturbation treatment by adding terms of the type $c_{\mu j}^2 m^{|\mu-\omega|} \delta A$, where $|\mu-\omega|$ is the 'distance' of the triple bond μ from a terminal bond ω. The parameters δA and m are those defined

above. Such a treatment yields: N = 1, $\Delta(1) = 2.30$ eV; N = 2, $\Delta(1) = \Delta(2) = 1.57$ eV; N = 3, $\Delta(1) = \Delta(3) = 1.07$ eV, $\Delta(2) = 1.30$ eV; N = 4, $\Delta(1) = \Delta(4) = 0.75$ eV, $\Delta(2) = \Delta(3) = 1.03$ eV. Comparison with the observed shifts given in *Figure 3* reveals that the agreement is as good as can reasonably be expected for such a crude model.

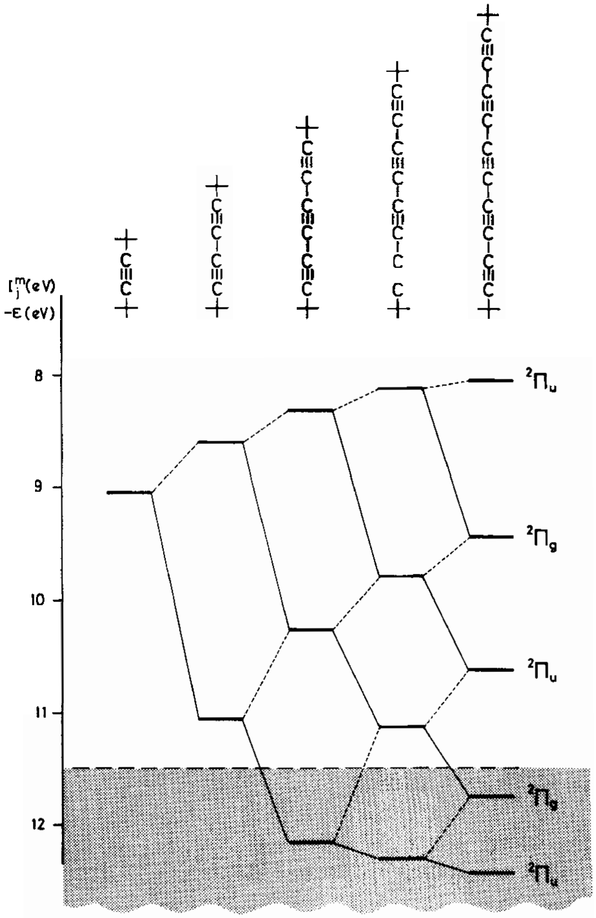


Fig. 2. *Correlation diagram of the $^2\Pi$-state energies of di-*t*-butylpolyacetylene radical cations* t-*Bu-*$(C{\equiv}C)_N$-t-*Bu*$^+$ *with N = 1 to 5*

The positions I_j^m of the corresponding band maxima can also be interpreted as orbital energies according to *Koopmans'* approximation $I_j^m = -\varepsilon_j$. Unbroken lines connect states with the same symmetry label. The shaded area corresponds to the energy region occupied by the band system due to electron ejection from the *t*-butyl groups.

(4) To conclude, we compare in *Figure 4* the shifts Δ(j) induced by terminal alkyl groups R on the band positions of the photoelectron spectra of di- and triacetylenes **2**(2) and **2**(3). The data for R ≠ *t*-butyl are taken from references [4] and [5]. It is of interest that the ionization energy gap between the first and the

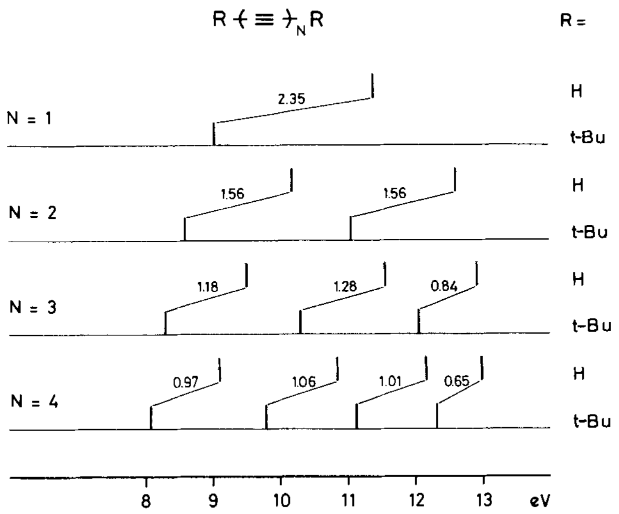


Fig. 3. *Shifts Δ(j) of the π-bands due to substitution by* t*-butyl-groups* (see formula (1))

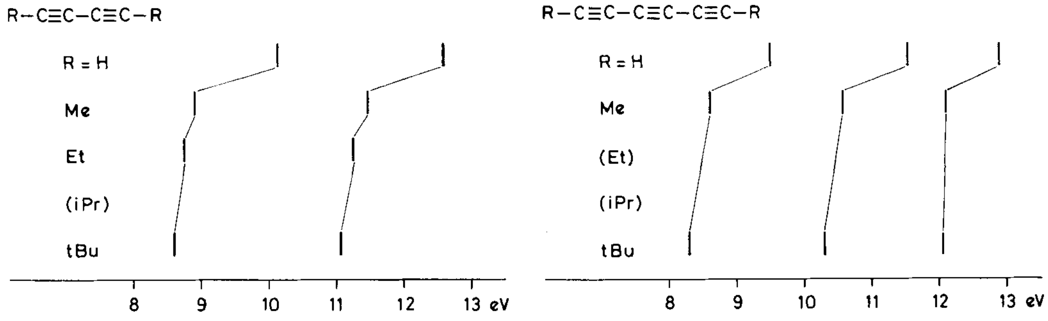


Fig. 4. *Shifts induced by alkyl-groups in the π-band positions of dialkyldiacetylene and dialkyltriacetylene*

second (third) band in the spectra of di-R-diacetylenes (di-R-triacetylenes) does not depend significantly on R:

	$R-(C{\equiv}C)_2-R$	$R-(C{\equiv}C)_3-R$	
R=H	2.5 eV	3.4 eV	(4)
Me	2.6 eV	3.5 eV	
Et	2.5 eV		
t-Bu	2.5 eV	3.7 eV	

In a previous publication [5] we have drawn attention to this fact which seems to contradict a general rule [9], namely that the shift induced by alkyl substituents R in the position I_j^m of a given band j of the unsubstituted parent compound should be larger, the higher the original I_j^m value. The rationale behind this rule may be found in second order perturbation theory applied to a model which emphasizes the hyperconjugative interaction of the alkyl groups with the π-orbitals to be perturbed. (An example for the working of this rule is provided by the correlation diagram of *Figure 13* in [10]). Obviously, the above rule suffers from exceptions. If true, one would expect that the gaps listed in (4) should decrease from H to *t*-Bu. If anything, there is a slight tendency for them to increase. Such exceptions are due to the fact that the influence of alkyl groups on ionization energies is more complex than usually assumed and that apart from inductive and/or hyperconjugative mechanisms one must also consider the participation of R in the electronic relaxation process which accompanies the ejection of an electron.

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