68. The Electronic States of the Pentatetraene Radical Cation

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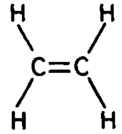
Summary

HeIα excited photoelectron spectra of pentatetraene and the inferred ionization energies are reported. The first band has a characteristic *Franck-Condon* envelope similar to the first photoelectron bands of allene and butatriene. The four bands found below 16 eV ionization energy have been assigned to the $\tilde{X}^2E$, $\tilde{A}^2E$, $\tilde{B}^2E$ and $\tilde{C}^2B_2$ states of the radical cation of pentatetraene by comparison with *STO-3G* and *SPINDO* calculations on the cumulene series. The correlation scheme includes the 2*s* shell ionization energies of ethylene, allene and butatriene. The π-orbital ionization trends of the cumulenes are discussed in the framework of localized orbitals calculated with the *STO-3G* basis set.

A synthesis has recently been developed [1] for pentatetraene, C_5H_4 (**4**). In this paper we report its photoelectron spectrum and compare it with those of the lower homologues in the cumulene series, ethylene [2–4], allene [3] [5] and butatriene [6].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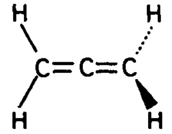
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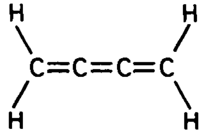
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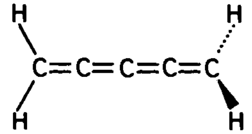
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Photoelectron Spectrum of Pentatetraene. – The photoelectron spectrum shown in Fig. 1 was recorded on a modified *Perkin-Elmer* photoelectron spectrometer based on the *Turner* design [7] ($\pi/\sqrt{2}$ cylindrical electrostatic condenser analyser of 5 cm radius) using He(Iα) radiation for excitation. The spectrum shown in Fig. 1 was recorded in the usual mode by incrementing linearly the voltage on the analyser plates. The resolving power was set at ≈ 150. The expanded recording of band ①,

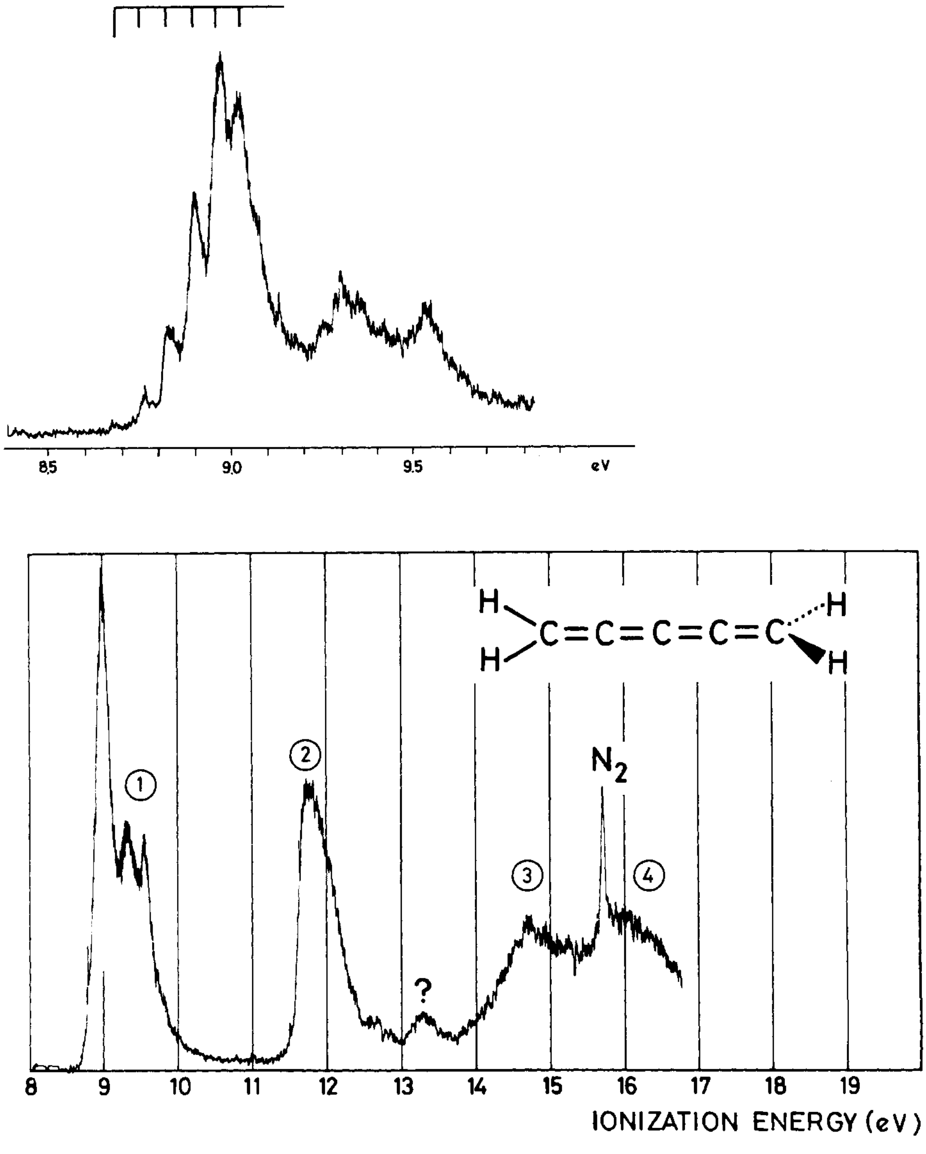


Fig. 1. *He(I) – Photoelectron spectrum of pentatetraene* (**4**). The upper spectrum is an expanded high resolution recording of band ①

shown in the upper part of Fig. 1, was recorded with a constant resolution, $\Delta E \approx$ 20 meV, by setting the analyser to collect 5 eV electrons, and preretarding the electrons by a linear voltage ramp. The samples of pentatetraene were prepared on a $\approx$ 50 mg scale by pyrolysis of the vinylallene precursor as described [1], and were purified by gas-chromatography. Adiabatic and vertical ionization energies, as well as estimates of the dominant vibrational spacings, are summarized in Tab. 1.

Table 1. *Adiabatic* ($I_{a,j}$) *and band maximum* ($I_{m,j}$) *ionization energies of pentatetraene.* Ionization energies in eV: Mean error ± 0.02 eV for band ①; ± 0.1 eV for bands ②, ③ and ④

State	Band	$I_{a,j}$	$I_{m,j}$[b])
$\tilde{X}={}^2E$	①	8.67	8.99[a])
$\tilde{A}={}^2E$	②	11.55	11.8$_5$
$\tilde{B}={}^2E$	③		14.6
$\tilde{C}={}^2B_2$	④		15.8

[a]) 9.1$_5$ eV corresponds to the centroid of the *Jahn-Teller* distorted band.
[b]) Position of the band maximum.

Four bands are apparent in the photoelectron spectrum of **4** below 16 to 17 eV ionization energy. The small peaks between 12.5 and 13.5 eV are probably due to an unknown impurity, which may originate as result of decomposition of **4**. The contour of band ① is similar to that of the first band in the allene spectrum [3] [5], both radical cations $\mathbf{4}^+$ and $\mathbf{2}^+$ undergoing a *Jahn-Teller* distortion [3] [8] in their electronic ground states $\tilde{X}(^2E)$. This leads to the characteristic *Franck-Condon* envelope [9] which, however, is observed for the first band in the photoelectron spectrum of butatriene as well [6]. A rather narrow intense band is followed by subsidiary band(s) and the vibrational frequencies discernible on the leading band are 700 cm^{-1}, 540 cm^{-1} and 590 ± 80 cm^{-1} in the case of allene [3], butatriene [6] and pentatetraene respectively.

The maximum of band ① occurs at $I_{m,1}=8.99$ eV, but the vertical ionization energy $I_{v,1}$ corresponding to the transition from **4** in its equilibrium structure to the ground state radical cation $\mathbf{4}^+$ without changes in internal coordinates, is more correctly assigned to the centroid of band ①, which is estimated to lie around 9.2 eV. Band ② in the spectrum of **4** corresponds to the $\tilde{A}(^2E)$ state of the radical cation which is again a *Jahn-Teller* unstable state. The position of the centroid of band ② is 11.8$_5$ eV.

The third band ③ in the photoelectron spectrum of **4**, $I_{v,3} \approx 14.6$ eV is due to the removal of an electron from the 1e(π) orbitals which are heavily centred on the methylene pseudo-π orbitals. A fourth band, which corresponds to ionization from a non-degenerate orbital *i.e.* the out-of phase combination of the CC-σ-orbitals, is

Table 2. *Optimized STO-3G geometries and total energies of ethylene* (**1**), *allene* (**2**), *butatriene* (**3**) *and pentatetraene* (**4**)

Molecule [Ref.]	Symmetry	Bond lengths (Å)			H–C–H angle	Energy (a.u.)
		C(1)=C(2)	C(2)=C(3)	H–C(1)		
1 [12]	D_{2h}	1.306	–	1.082	115.6°	− 77.07396
2 [13]	D_{2d}	1.288	–	1.083	116.2°	−114.42172
3 [6]	D_{2h}	1.296	1.257	1.085	115.9°	−151.77399
4	D_{2d}	1.295	1.264	1.084	116.1°	−189.12968

apparent around 16 eV. A further band is predicted to overlap band ④, according to the *STO-3G* and the *SPINDO* calculations (Tab. 3).

Molecular Orbital Calculations. – In order to aid in assigning the spectrum, calculations were carried out using the semiempirical *SPINDO* procedure [10] and the *ab initio STO-3G* minimal *Gaussian* basis set [11]. In both cases the geometry used was that obtained by full optimization (within D_{2d} symmetry) of **4** at the *STO-3G* level. The optimized geometry is given in Tab. 2, where the previously-calculated *STO-3G* geometries of **1** [12], **2** [13] and **3** [6] are also tabulated.

There is considerable variation in the lengths of C=C double bonds in the cumulene series. In allene, the bonds are shorter than in ethylene (1.288 *vs.* 1.306 Å) due to the *sp*-hybridization at the central carbon atom in allene. In butatriene and pentatetraene, the central C=C bonds involve two *sp* carbon atoms, and are thus shorter still (1.257 and 1.264 Å, respectively). Geometry optimization of the *STO-3G* models of the radical cations $\mathbf{1}^+$ [12] and $\mathbf{3}^+$ [6] in their electronic ground states $\tilde{X}(^2B_{2u})$ and $X(^2B_{3g})$ respectively suggest that significant distortion occurs in these systems upon ionization. A similar effect is expected for **4**, but calculations on $\mathbf{4}^+$ were not carried out.

Table 3. *Observed* ($I_{m,j}$) *and calculated ionization energies of ethylene* (**1**), *allene* (**2**), *butatriene* (**3**) *and pentatetraene* (**4**). For convenience the symmetry labels of **1** are those given in ref [4].

Molecule	Orbital	$I_{m,j}$ (eV)	Orbital energy		$I_{v,j}$ predicted (eV)	
			STO-3G (a.u.)	SPINDO (eV)	STO-3G (cf.(1))	SPINDO (cf.(2))
1 (D_{2h})	$1b_{2u}$	10.51 [2]	-0.33550	-10.62	10.26	10.83
	$1b_{2g}$	12.85 [2]	-0.45799	-12.07	12.77	12.31
	$3a_g$	14.66 [2]	-0.54033	-14.56	14.47	14.86
	$1b_{3u}$	15.87 [2]	-0.60552	-15.64	15.80	15.96
	$2b_{1u}$	19.1 [2]	-0.74577	-18.45	18.69	18.84
	$2a_g$	23.7 [15]	-0.98762	-24.15	23.66	24.66
2 (D_{2d})	2e	10.02 [5]	-0.32332	-10.00	10.01	10.20
	1e	14.75 [15]	-0.56490	-14.53	14.97	14.83
	$3b_2$	15.4 [5]	-0.56700	-15.12	15.01	15.43
	$4a_1$	17.3 [5]	-0.66319	-16.82	16.99	17.17
	$2b_2$	22.0 [16]	-0.90039	-22.10	21.86	22.57
	$3a_1$	24.4 [16]	-1.01672	-24.29	24.25	24.81
3 (D_{2h})	$1b_{3g}$	9.30 [6]	-0.27221	-9.18	8.96	9.36
	$2b_{3u}$	9.98 [6]	-0.30906	-9.56	9.71	9.75
	$1b_{2u}$	11.78 [6]	-0.43310	-12.16	12.26	12.40
	$1b_{2g}$	14.2 [6]	-0.55583	-14.08	14.78	14.37
	$1b_{3u}$	15.0 [6]	-0.58089	-14.13	15.30	14.42
	$5a_g$	15.5 [6]	-0.58239	-14.95	15.33	15.26
	$4b_{1u}$	16.5 [6]	-0.63295	-15.69	16.37	16.01
	$4a_g$	20.6 [16]	-0.82643	-17.77	20.34	18.14
	$3b_{1u}$	23.0 [16]	-0.95501	-21.67	22.99	22.13
	$3a_g$		-1.02869	-24.02	24.50	24.53
4 (D_{2d})	3e	9.15	-0.26591	-8.91	8.83	9.08
	2e	11.7	-0.43155	-11.94	12.23	12.18
	1e	14.6	-0.57299	-14.64	15.14	14.94
	$5b_2$	15.8	-0.59280	-15.64	15.54	15.96
	$6a_1$		-0.62036	-15.97	16.11	16.30
	$4b_2$		-0.77319	-19.71	19.25	20.12
	$5a_1$		-0.90022	-21.92	21.86	22.38
	$3b_2$		-0.98913	-23.55	23.69	24.05
	$4a_1$		-1.03950	-24.45	24.72	24.97

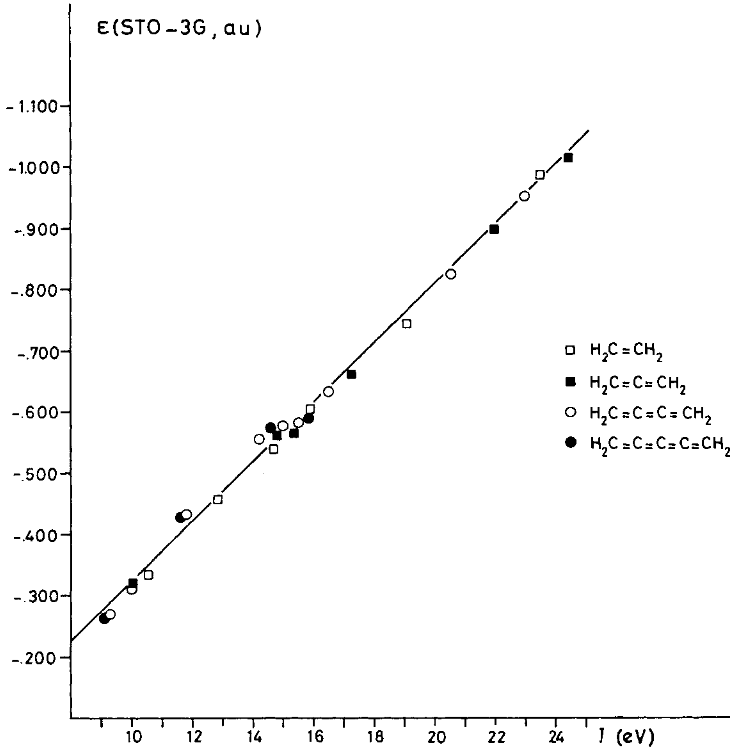


Fig. 2. *Least-squares linear regression plot of the* STO-3G *orbital energies, ε_J, versus the experimental ionization energies, $I_{m,j}$, for the cumulenes*

STO-3G and *SPINDO* orbital energies for the molecules **1** to **4** are given in Tab.3. It has been previously shown [6] [14] that such values yield excellent correlations with the observed ionization energies of unsaturated hydrocarbons if *Koopmans'* approximation is invoked. The present systems are no exception. In Fig. 2, *STO-3G* orbital energies ε_j are plotted against observed ionization energies $I_{m,j}$ including the data for the 2*s*-shell ionization of **1** [15], **2** and **3** [16]. When the *STO-3G* orbital energies are expressed in eV the following linear regression is obtained by the standard least-squares technique:

$$\varepsilon_j^{\text{STO-3G}}\,(\text{eV}) = 4.451 - 1.324\ I_{m,j}(\text{eV}) \qquad (1)$$

The corresponding regression, using the orbital energies from the SPINDO model is:

$$\varepsilon_j^{\text{SPINDO}}\,(\text{eV}) = -0.029 - 0.978\ I_{m,j}(\text{eV}) \qquad (2)$$

Using these regression lines, the 'predicted' $I_{v,j}$ values listed in the last two columns of Tab. 3 are obtained, from which it is seen that the agreement between theory and experiment is as good as can reasonably be expected. It is certainly adequate to be confident of the assignment proposed in Tab. 1 for 4^+.

π-Orbitals of Cumulenes. – In the following discussion we shall rely for convenience on the traditional assumption of *Koopmans'* approximation, namely that the observed vertical ionization energies can be equated with the negative orbital energies ε_j of the ground-state molecule: $I_{v,j} = -\varepsilon_j$. Using this approximation the π-levels of the molecules **1** to **4** are diagrammed in Fig. 3. These levels refer to two types of π-orbitals: (a) 'isolated' π-orbitals, as in ethylene ($1b_{2u}$), in allene (2e), or the second π-orbital (from the top) in butatriene ($2b_{3u}$); and (b) pairs of four-centre butadiene-like π-orbitals with in-phase ($1b_{2u}$ of **3**, 2e of **4**) and out-of-phase ($1b_{3g}$ of **3**, 3e of **4**) combination of the two-centre basis orbitals.

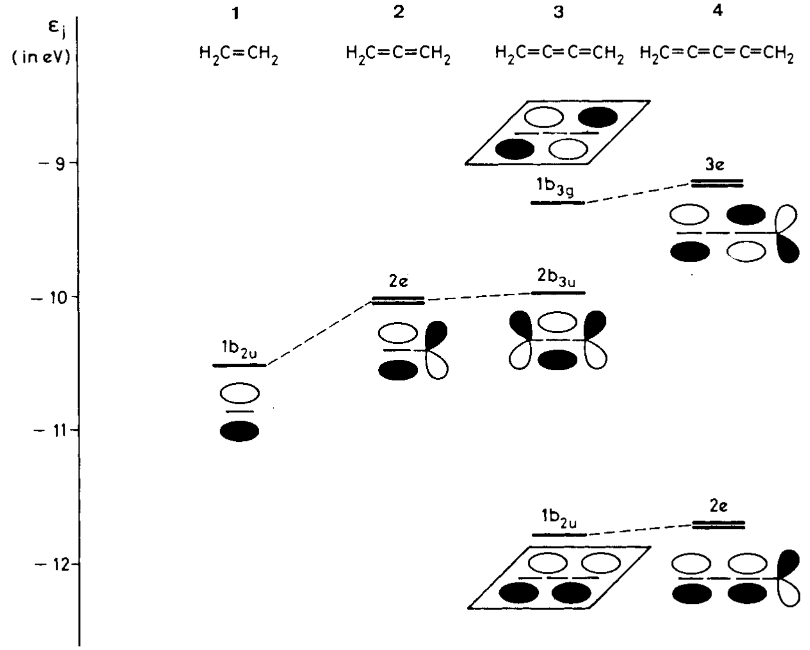


Fig. 3. *Correlation diagram of the π-orbitals of the cumulenes plotted by equating $I_{v,j} = -\varepsilon_j$.* The approximate descriptions of the molecular orbitals are schematically drawn. Concerning the symmetry label for **1**, see legend to Tab. 3.

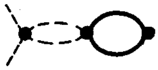
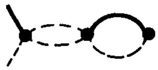
The 'isolated' π-orbitals are destabilized, going from **1** to **3**, which leads to a decrease of the corresponding ionization energies. However, this is not what one might naively have expected. With increasing *s*-character at the involved carbon atoms, π-bonds should become more acetylene-like and shorter, which they do (see Tab. 2), and the π-ionization energies should on this basis follow a trend opposite that observed: ethylene, $I_v(\pi) = 10.5$ eV; acetylene, $I_v(\pi) = 11.4$ eV [3]. Similarly, according to this hybridization argument, the mean of the orbital energies of each pair of four centre π-orbitals should shift down upon going from **3** to **4**; instead it is seen to shift slightly up.

A simple and instructive rationalization of the observed trends may be proposed on the basis of localized molecular orbitals (LMO, λ_j) [17]. The following discussion refers to LMO's calculated with the *STO-3G* basis set, and derived according to the

Foster-Boys localization procedure [18]; similar qualitative conclusions are reached using the *SPINDO* model together with the *Edmiston-Ruedenberg* criterion [17].

Localized orbitals λ_j, obtained by unitary transformation of the canonical molecular orbitals φ_j, are of two types in the present cases: CHσ bonding orbitals λ(CH),

Table 4. *Matrix elements* $\langle\lambda_i|\mathfrak{F}|\lambda_j\rangle$ *for the localized STO-3G orbitals* λ_i. A: self energies A(λ_i); B: Cross term B(λ_i, λ_j) between two geminal localized orbitals: Γ: Cross term $\Gamma(\lambda_i, \lambda_j)$ between two vicinal localized orbitals. The orbitals λ_i, λ_j to which the matrix elements refer are those indicated by heavy lines in the diagrams. All values are in eV

		1	**2**	**3**	**4**
A(λ_i)		-17,44	-17,61	-17.75	-17,84
		-16,05	-16,63	-16,66	-16,83
		---	-16,63	-17.21	-17.32
B(λ_i,λ_j)		-2,97	-2,85	-2,91	-2,87
		-2,34	-2,34	-2,32	-2,33
		-6,92	-7,22	-7,07	-7,12
		---	-1,66	-1,64	-1,63
		---	-7,22	-7,56	-7,43
Γ(λ_i,λ_j)			-0,79	-0,81	-0,75
			1,12	1,15	1,09
				-0,95	-0,97
				1,24	1,27

and (CC) 'banana' bonds λ(CC). The elements of the *Hartree-Fock* matrix in the LMO basis are defined as $F_{\lambda,ij} = \langle \lambda_i | \mathfrak{F} | \lambda_j \rangle$ where $\mathfrak{F}$ is the *Fock* operator. Of these we take into account three types of matrix element: (1) the selfenergies of the localized λ(CH) and λ(CC) orbitals, $A(\lambda_i) = F_{\lambda,ii}$; (2) the 1,2 interaction elements $B(\lambda_i, \lambda_j)$ for geminal bond orbitals λ_i and λ_j; and (3) the 1,3 interactions $\Gamma(\lambda_i, \lambda_j)$ for vicinal bonds λ_i and λ_j. Longer-range interactions have been neglected. *STO-3G* values for the specified matrix elements A, B, and Γ are collected in Tab. 4.

Using only the λ(CC) banana orbitals it is possible to calculate energies for the 'pure' π-orbitals of the molecules **1** to **4**. For example, in the case of allene two equivalent λ(CC) banana bonds (A(CC) = −16.63 eV) are mixed under the influence of the appropriate interaction term (B(CC, CC) = −7.22 eV), leading to an in-phase σ combination at −23.85 eV and an out-of-phase 'pure π' combination at −9.41 eV. The corresponding π-orbital of ethylene lies at −9.13 eV in the *STO-3G* approximation, so that there is indeed a downward shift going from **1** to **2** as anticipated on the basis of the above hybridization arguments.

However, in allene there exists the additional possibility of hyperconjugative interaction between the 'pure π' orbitals and the in-plane pseudo-π orbitals of the CH_2 groups, as originally proposed by *Mulliken* [19]. The two equivalent λ(CH) orbitals (A(CH) = −17.61 eV) combine through the appropriate interaction element (B(CH, CH) = −2.85 eV) to form a pseudo-π methylene combination at −14.76 eV. The net interaction between this combination and the pure π-orbital is found from the '*cis*' CC ... CH interaction (B(CC, CH) = −0.79 eV, Tab. 4) and the '*trans*' (B(CC, CH) = 1.12 eV) to be $B_{net} = -1.91$ eV. This leads to a highest occupied π-orbital, which involves now hyperconjugation, at −8.80 eV, above that of ethylene, in accord with the experimental observation.

Similar analyses of **3** and **4** have been carried out, and it is found that pure π levels shift down in orbital energy when sp^2 centres are replaced by *sp*. From the results summarized in Fig. 3 and from the numerical values given in Tab. 3 it is evident that the change in the orbital energy of the 'isolated' π-orbital(s) $1b_{2u}(\pi)$ in **1**, $2e(\pi)$ in **2** and $2b_{3u}(\pi)$ in **3** displayed in Fig. 3 is the resultant of two effects: a) a lowering of the orbital energy of the pure π-orbital, mainly due to the change in A(CC) (see Tab. 4) and b) a strong destabilizing influence of the terminal CH_2 group which overcompensates the negative shift of the π-orbital with which they interact. The latter effect is especially pronounced in the $2b_{3u}$ level of butatriene, in which the central π-bond interacts with two in-plane methylene groups. The true hyperconjugative destabilization is considerably larger than suggested by the experimental values plotted in Fig. 3. Going from **3** to **4** destabilizing effect of the pseudo-π CH_2 orbitals is necessarily less important, the π-orbitals extending over four centres. In all cases the consideration of 1,2 and 1,3 interactions alone reproduces well the full *ab initio* results from which it may be concluded that long-range interactions are of negligible importance in these simple π-systems.

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