125. Cross Conjugated Polyenes Derived from 2-Vinyl-butadiene: Electronic States of their Radical Cations, and Triplet Energy[1])

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Dedicated to Professor *Jack D. Dunitz* on the occasion of his 60th birthday

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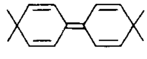
Summary

The doublet states of the radical cations of the cross conjugated polyenes 4,4-dimethyl-1-methylidene-2,5-cyclohexadiene **2** and its bis-derivative **1** have been investigated by photoelectron spectroscopy and by electronic spectroscopy of $\mathbf{1}^{+}$, prepared at 77 K in an electron scavenging matrix by γ-irradiation. Simultaneous consideration of the spectral results shows $\mathbf{1}^{+}$ to be the second hydrocarbon molecular cation (after 2,2-dimethyl isoindene) which possesses a first excited doublet state (D_1) of non-*Koopmans* nature ($^2B_{3g}$). The first *Koopmans*-type excited state ($^2B_{2g}$) expected from PE. spectroscopy lies, however, very close in energy. In addition T_1 of **1** was observed by electron energy loss spectroscopy at 2.0±0.1 eV. Application of the 'SDT-equation' predicts for this state only 1.05 eV; there is at present no reasonable explanation for this failure.

Introduction. – We have been interested for some years in the electronic structure [1–3] and the thermochemical properties [4] of cross-conjugated olefins and their radical cations. The latter often revealed unusual and interesting features such as spontaneous double-bond distortion [2] or low-lying non-*Koopmans* states [3]. Recently **1**, a new member of this family of compounds, was synthesized [5] and subjected to extensive structural [6], spectroscopic [7], and theoretical [8] investigations. This paper communicates an extension of these studies to the corresponding radical cations. Furthermore the vertical triplet energy of **1** (which shows no phosphorescence) was determined using a recently developed electron spectrometer [9].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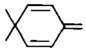
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[1]) Part XI of Studies of Molecular Ions. Part X: [20].

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Thus we initiated an investigation of **1** using the various techniques described in the *Experimental Part.* We also include the PE. spectrum of the related hydrocarbon **2** [5].

Experimental. – PE. spectra were obtained on a modified *PE 16* instrument incorporating a preretardation device allowing spectra to be obtained at 20–25 meV resolution [10] (see fwhm of first peak of **2**). Several hundred scans were accumulated on a *Canberra* multi-channel analyzer interfaced to a *PDP 11/34* computer for data workup. Internal calibration was done with Ar/Xe and CH_3I.

Electronic absorption (EA.) spectra of the radical ions were obtained using techniques pioneered mainly by *Shida & Iwata* [11]. Glassy, frozen solutions of the polyenes (10^{-3} M) in a *Freon* mixture [12] contained in 10 mm copper cuvettes with *Suprasil* windows were exposed to 1.3 MeV γ-radiation from a ^{60}Co-source (0.3 Mrad/h) for 1 h. Subsequent transfer into a quartz *Dewar* inside a *PE 330* UV./VIS./NIR. spectrometer was effected under N_2 to avoid fogging of the cuvette windows. Optical spectra were recorded on an *Apple II+* computer interfaced to the *PE 330* and to the *PDP*-computer where spectral data were worked up similarly to the PE. data.

Electron energy loss (EEL.) spectra were obtained on the facility described in [9] where **1** was introduced through a heated inlet system at 120°. For the PPP calculations we employed a program based on the parametric expressions proposed by *Zahradnik et al.* [13]. For triplet states, the special parameters described in [14] were used while calculations on radical ions were done with the open shell procedure based on the *Longuet-Higgins/Pople*-formalism [15] with parameters according to *Zahradnik & Čársky* [16]. Bond lengths and bond angles were fixed at 140 pm and 120°, respectively, but in all cases the variable β procedure [13] was used which in our experience gives better agreement with experimental transition energies.

Results and discussion. – *PE. spectra. Figure 1* presents the PE. spectra of **1** and **2** in the range amenable to interpretation. *Table 1* lists the exact peak positions (including vibrational progressions where resolved) along with a HMO π-orbital scheme and the calculated ionization energies from the parametric relationship [17]:

$$I_{v,i}(\text{eV}) = 6.553 + 2.734\, x_i\, (\beta\text{-units}) \qquad (1)$$

Assignment of the first four bands of **1** and the first two of **2** is straightforward on the basis of simple *Hückel* theory. Also, the observed $I_{v,i}$ correlate well with those obtained from the simple parametric relationship *1*[3]).

Interestingly, any attempt to improve the quantitative correlation by using the more sophisticated HMO-based parametric treatments accounting for first-order bond fixation in polyenes [17] failed. For example the excited states ^2A_u and $^2B_{2g}$ of $\mathbf{1}^+$ lie very close to the corresponding pair of states in related biphenyl (which has the same second and third HMO π-orbitals as **1** lying at −9.05 eV [19]). However, first-order bond fixation has very little influence in the case of biphenyl (predicted $I_{v,2} = 9.22$ eV) but shifts the degenerate pair of states in **1** to 10.00 eV. The inductive effect of the CMe_2-bridges in **1** can at most account for half of this unusually large discrepancy because the $^2B_{1u}$ ground state of $\mathbf{1}^+$ is (unlike $^2A_u/^2B_{2g}$) affected both inductively and hyperconjugatively by this perturbation, and is predicted at 7.50 eV, *i.e.* only 0.45 eV too high. We can offer no explanation for this breakdown of the first-order bond-fixation model.

Regarding the HMO degenerate pair of states ^2A_u and $^2B_{2g}$ in **1** we note a ≈0.2 eV split in the corresponding PE. bands. This may be due to the transannular

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[3]) A statistical analysis of $I_{v,i}$(exp.) *vs.* $I_{v,i}$(calc.) of **1** and **2** yields a correlation coefficient of 0.990 with a straight line intersecting the ordinate at −0.18 eV. While this does not imply that simple HMO is an excellent model [18] it serves as a nice example of how a simple model may be better than a more sophisticated one (see following paragraph).

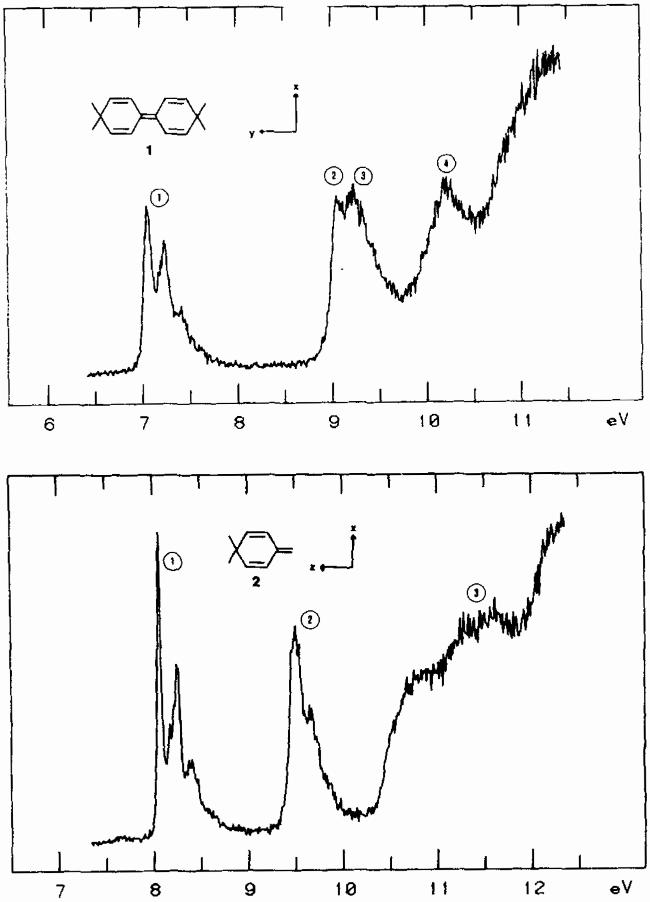

Fig. 1. *PE. spectra of* **1** *and* **2** (Circled figures correspond to peak numbers in *Table 2*)

interactions which are antibonding in the former and bonding in the latter state (see orbital pictures in *Table 1*).

EA. spectrum of $\mathbf{1}^+$. In contrast to **2**[4]), a frozen solution of **1** in the *Freon* mixture exposed to ≈ 0.3 Mrad of γ-radiation gives a well-resolved spectrum of $\mathbf{1}^+$ as shown in *Figure 2*.

At first sight, this spectrum stand in excellent accord with what one expects from the PE. spectrum of **1**: $\lambda_{\max} = 618$ nm for $\mathbf{1}^+$ matches with $I_{v,2} - I_{v,1} = 2.02$ eV for **1**. The same is true for the second optical transition at 398 nm $\hat{=}$ 3.12 eV, given $I_{v,4} - I_{v,1} = 3.18$ eV. Nevertheless, we propose a different assignment of the first electronic transition of $\mathbf{1}^+$ on the basis of the following arguments.

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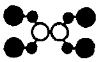
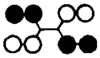
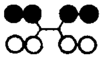
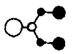
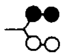
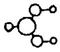
[4]) Compound **2** gives only very broad and featureless absorption upon γ-irradiation in frozen *Freon* mixture, indicating the absence of discrete $\mathbf{2}^+$ which should show a clear $^2B_1 \leftarrow {}^2A_2$ transition at 1.4 eV $\hat{=}$ 885 nm. Presumably some interaction with the solvent leads to a new species displaying no spectroscopically traceable relation to $\mathbf{2}^+$.

Table 1. *Measured and calculated ionization energies of* **1** *and* **2**

Comp.	Peak i	$I_{v,i}$(exp.)[a] (eV)	$I_{v,i}$(HMO)[b] (eV)	ε_i(HMO) (β)	ψ_i(HMO)	Symmetry[c]
1	①	7.05 (7.23) (7.40)	7.38	−0.311		B_{1u}
	②	9.07	9.29	−1.0		A_u
	③	9.24	9.29	−1.0		B_{2g}
	④	10.23	10.42	−1.481		B_{3g}
2	①	8.07 (8.27) (8.4)	7.97	−0.518		B_1
	②	9.47 (9.64)	9.29	−1.0		A_2
	③	11.4	11.81	−1.923		B_1

[a] Figures in brackets denote vibrational progressions. [b] Calculated using the parametric relationship *1*. [c] Point group: D_{2h} for **1**, C_{2v} for **2**. The corresponding symmetry species in D_2 (C_{2h}) point group for **1** are obtained by dropping the subscript letters (numbers). The axes are chosen as indicated in *Figure 1*.

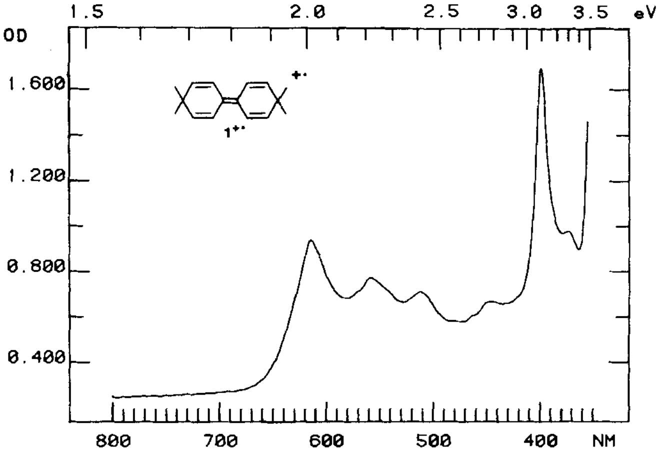


Fig. 2. *EA. spectrum of* $\mathbf{1}^{+}$ (At $\lambda < 350$ nm the parent neutral starts strongly absorbing)

Group theory requires that the (first) $^2A_u(\pi_2) \leftarrow {}^2B_{1u}(\pi_1)$[5]) *Koopmans* transition be electric dipole forbidden in the D_{2h}-point group[6]). Only the second *Koopmans* transition $^2B_{2g}(\pi_3) \leftarrow {}^2B_{1u}(\pi_1)$, expected at 2.19 eV ($\triangleq$566 nm) from the PE. spectrum, is dipole allowed but polarized along the short axis (x) of **1**$^+$. However, if the observed 618-nm band were assigned to this latter transition a solvent shift of 0.27 eV would result, which is too large for this ion with its a well-delocalized charge (*cf.* [21] [22]).

Recourse to theory resolves the problem. A simple HMO configuration diagram taking into account virtual orbitals *(Fig. 3)* reveals that the lowest excited configuration corresponds to the Homo → Lumo non-*Koopmans* transition $^2B_{3g}(\pi^*_{-1}) \leftarrow {}^2B_{1u}(\pi_1)$ which is dipole-allowed and y-polarized. Still on the HMO level, we calculate [23] that its oscillator strength is three times that for $^2B_2g(\pi_3) \leftarrow {}^2B_{1u}(\pi_1)$. Hence, the corresponding EA. band should clearly dominate the spectral region in question. PPP-CI-calculations *(Fig. 3)* confirm these expectations although quantitative agreement with experimental results (dashed lines) is not very satisfactory.

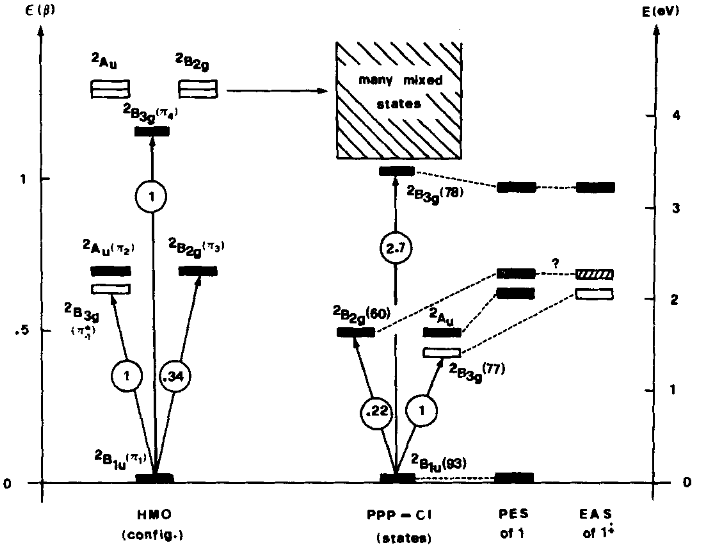


Fig. 3. *Theoretical and experimental configuration* (state) *diagramm of* **1**$^+$ (Solid bars denote *Koopmans* configurations (states), open bars non-*Koopmans* configurations (states). Circled figures are relative calculated oscillator strengths for electronic transitions. Figures in brackets indicate percentage of leading configuration in the CI-expansion)

With respect to the *Koopmans* transition $^2B_{2g}(\pi_3) \leftarrow {}^2B_{1u}(\pi_1)$ which therefore is not responsible for the peak at 618 nm *(Fig. 2)*, we conclude that it is buried in

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[5]) We make use of the notation introduced in [20] where the expression in the brackets indicates the singly occupied MO. The numbering scheme for the π-orbitals is defined in *Table 1*.

[6]) These selection rules persist also upon descent to C_{2h}-symmetry, shown by **1** in the gas-phase [6a] and the crystal [6b] (and therefore presumably also in solution). Only if torsion around the central bond occurs ($D_{2h} \rightarrow D_2$) does the $^2A_{(u)} \leftarrow {}^2B_{1(u)}$ transition become electric dipole allowed, and polarized along the z-axis, hence associated with a weak transition moment.

the train of vibrational progressions following it, being perhaps responsible for the somewhat odd spacings observed (1660 and 1790 cm^{-1}). Concerning the second band at 398 nm[7]) we are confident in assigning it to $^2B_{3g}(\pi_4) \leftarrow {}^2B_{1u}(\pi_1)$ even though a large number of strongly mixed states are predicted by PPP-CI to lie in the spectral region concerned. However, from the same calculations none of these states is accessible *via* a transition with a comparable oscillator strength to the one above.

EEL. spectra. – Triplet energy of **1**. Having identified the Homo→Lumo transition in $\mathbf{1}^+$ (corresponding to its lowest excited doublet energy D_1) and given the same transition in **1** [7] (corresponding to S_1), we are able to estimate the vertical triplet energy T_1 of **1** *via* the 'SDT-equation' [3] [20]:

$$D_1 = (S_1 \cdot T_1)^{1/2} \qquad (2)$$

Equation 2 should apply in the present case (alternant hydrocarbon, 'paired' orbitals involved) provided that the excited states in question are all reasonably well-described by the Homo→Lumo excited configuration. Our PPP-CI-calculations indicate that this is the case *(Table 2)*. Using the experimental values $\lambda_{max}(\mathbf{1}) = 319$ nm (gas-phase value [7]) and $\lambda_{max}(\mathbf{1}^+) = 618$ nm, we arrive at:

$$E_T(\mathbf{1}) = \frac{E_D(\mathbf{1})^2}{E_S(\mathbf{1})} = \frac{(2.02)^2}{3.89} = 1.05 \text{ eV} \qquad (3)$$

Table 2. *PPP-CI-calculations for the first excited states of* **1** *and* $\mathbf{1}^+$

Species	State	Energy above ground state	% HOMO→LUMO configuration
1	$S_1(^1B_{2u})$	3.98 eV (319 nm)	98.5
	$T_1(^3B_{2u})$[a])	1.14 eV (1090 nm)	94.1
$\mathbf{1}^+$	$D_1(^2B_{3g})$	1.42 eV (873 nm)	76.6[b])

[a]) PPP triplet parameters. [b]) Most of the remaining 23.4% are higher excited C-type configurations (doubly occ. to virtual orbital promotion) which make up 40 of the 50 configurations in the present CI-treatment. A calculation without these gives a 90% pure Homo→Lumo state.

To test this prediction we subjected a frozen solution of **1** in isopropanol to emission spectroscopy. While the reported fluorescence of **1** [8] was clearly visible, we could detect no delayed emission (phosphorescence).

Therefore we applied the technique of EEL. spectroscopy as described recently by *Allan* [9] to detect T_1 of $\mathbf{1}(^3B_{2u})$ in the gas-phase. *Figure 4* shows the EEL. spectrum of **1** at different residual e^--energies.

As outlined in [9], the EEL. spectrum at high residual e^--energy should be nearly identical to the EA. spectrum of **1**, which is indeed the case ($S_1 = 3.89$ eV, *Fig. 4;* $S_1 = 319$ nm $\triangleq$ 3.89 eV [7]). At low residual energies (<4 eV) a new spectral feature

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[7]) The small band at ≈450 nm does *not* belong to $\mathbf{1}^+$ because it behaves differently from the other bands upon bleaching by visible radiation or bulk warming.

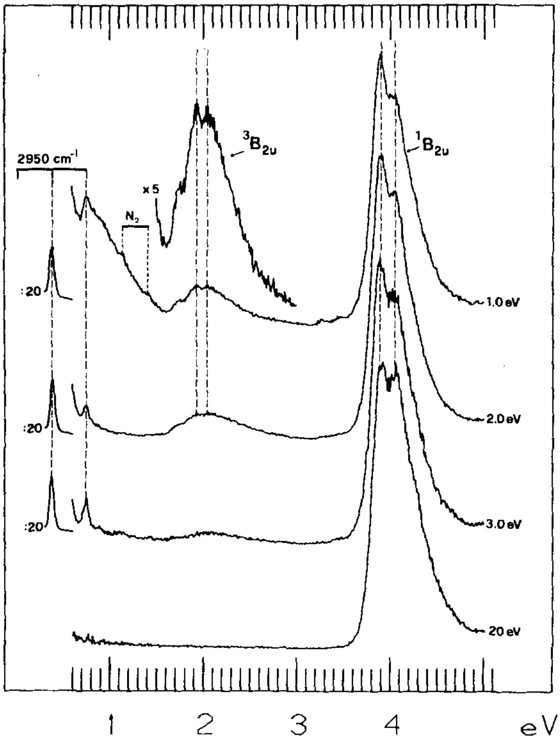

Fig. 4. *EEL. spectra of* **1** (Figures to the right indicate residual electron energy at which the spectrum was recorded. The 2950 cm^{-1} progression (first peak attenuated by a factor of 20) corresponds to excitation of a vibration of ground state **1**)

peaking at 2 eV begins to emerge, along with vibrationally highly excited states of the electronic ground state of **1**. The expanded inset at the top of *Figure 4* shows that the vertical transition occurs at 2.0±0.1 eV. We conclude that this band corresponds to the lowest triplet state T_1 of **1**. This is supported by the PPP-procedure *(Table 2)* which yields $T_1 = 1.14$ eV but has been found to consistently underestimate vertical triplet energies of polyenes by 0.7–1.3 eV [24]. We have at present no explanation for the failure of expression (*2*) which has been previously applied successfully [3] [20].

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