203. The Photoelectron Spectrum of Dibenzo-*p*-quinodimethane

by **Michael Allan**[1]), **Edgar Heilbronner**[1]) and **Gerd Kaupp**[2])

Physikalisch-chemisches Institut der Universität Basel, Klingelbergstrasse 80, CH–4056 Basel, und

Chemisches Laboratorium der Universität Freiburg i. Br., Albertstrasse 21, D–7800 Freiburg i. Br.

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Summary. The lowest states of dibenzo-*p*-quinodimethane radical cation are $^2B_{1u}$ (7.95 eV); $^2B_{2g}$ (8.66 eV); [$^2B_{3g}$, ^2A_u, unresolved] (9.1 eV); [$^2B_{1u}$, $^2B_{2g}$, unresolved] (10.7 eV). This confirms the assignment proposed by *Koenig et al.* [1] for the states of *p*-quinodimethane radical cation.

In a remarkable piece of work *Koenig et al.* [1] recorded and analysed the photoelectron spectrum of *p*-quinodimethane (**1**) which exhibits two bands at 7.87 $\pm$ 0.05 and 9.7 $\pm$ 0.1 eV with an integrated intensity ratio of 1:1.2. These have been interpreted as being associated with the radical cation doublet states $^2B_{1u}$ and $^2B_{3g}$, $^2B_{2g}$ of $\mathbf{1}^+$, respectively. (Note that the symmetry labels given in [1] differ from those used here because of an interchange in axes.)

As has already been shown by *Koenig et al.* [1], a naive LCBO (= Linear combination of bond orbitals) model calculation accounts rather nicely for the observed band pattern[3]). The necessary parameters (self-energies A_μ of the basis functions π_μ and interaction terms $B_{\mu\nu}$ for conjugated pairs π_μ, π_ν) can be derived as follows:

1) An investigation of *cis*- and *trans*-hexatriene (**2**) yielded $A_a = -10.25$ eV and $A_b = -9.99$ eV with $B_{ab} = -1.215$ eV [4]. Comparing A_a of **2** with $A_\pi = -10.51$ eV for ethylene we might expect that $A_a = -10.0$ eV is appropriate for the exocyclic π-orbital in **1**, whereas A_b should be the same for both molecules.

2) The analysis of the photoelectron spectra of fulvene (**3**) and of 3,4-dimethylenecyclobutene (**4**) [5] leads to $A_a = -10.3$ eV in **3** and **4**, and to $A_b = -10.2$ eV or -10.3 eV in **3** and **4** respectively.

3) The photoelectron spectra of the hydrocarbons **5**(n), *i.e.* **5**(0) = 1,4-cyclohexadiene to **5**(3) = 1,4,5,6,7,10,11,12-octahydronaphthacene [6] yielded $A_b = -10.3$ eV for all π-orbitals and a 'through-space' interaction term [7] $B_{bb'} = B_{b'b''} = \cdots = -0.5$ eV for each pair of 1,4-positioned double bonds.

Using the set of parameters $A_a = A_{a'} = -10.0$ eV, $A_b = A_{b'} = -10.3$ eV, $B_{ab} = \ldots = B_{a'b'} = -1.21_5$ eV, $B_{bb'} = -0.5$ eV for a LCBO description of the

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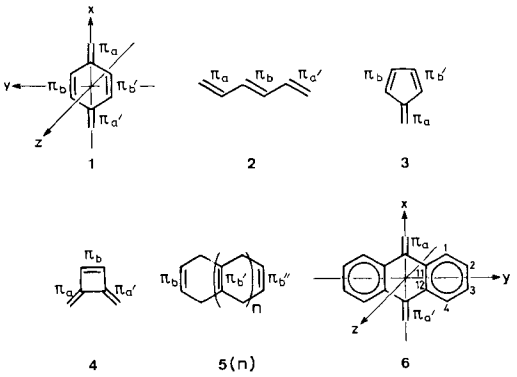
1) Basel.

2) Freiburg i. Br.

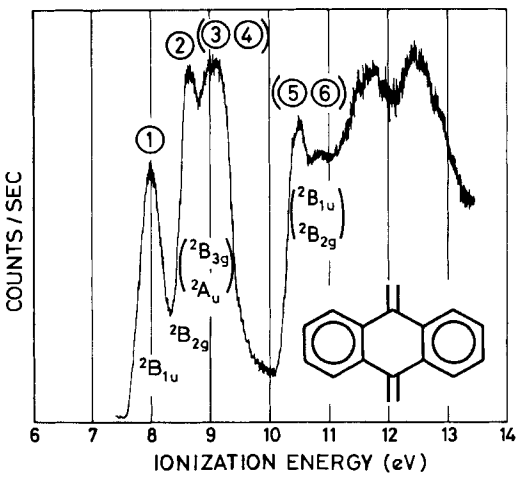
3) These authors use a somewhat different nomenclature, in which the basis functions of the linear combinations are named with reference to a pseudo valence bond scheme [2]. However, it can be shown that mathematically there is a complete one-to-one correspondence between the matrix elements used in their treatment and those of the more traditional LCBO-procedure [3].



π-system of **1** and making use of *Koopmans'* approximation we find the following ionization energies (in eV):

State of $\mathbf{1}^+$:	$I_{v,j}$(calc)	$I_{v,j}$(obs)[1]
$^2B_{1u}$	7.94	7.87 ± 0.05
$^2B_{3g}$	9.80	9.7 ± 0.1
$^2B_{2g}$	10.00	
$^2B_{1u}$	12.86	(12.5?)

The experimental value quoted for the second $^2B_{1u}$ state corresponds to the position of a large prominent feature near 12.5 eV which is probably due to the superposition of two (or more) bands.

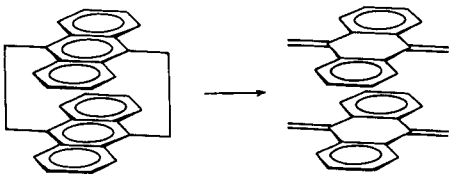


He(I)-Photoelectron spectrum of dibenzo-p-quinodimethane

Had we used $A_a = A_{a'} = -10.2$ eV instead of -10 eV, the $^2B_{2g}$ state would have shifted to 10.2 eV. Such a value is still acceptable for the following reason: Assuming *Koopmans'* approximation, electron ejection from the LCBO-orbital b_{2g}

puts half a positive charge on both exocyclic double bonds of **1**$^+$, leaving the population of the endocyclic double bonds unchanged. As has been pointed out in the case of the ionization energies of fulvenes [8] such a charge distribution leads to substantial electron rearrangement and thus to a stabilization of the $^2B_{2g}$ state, *i.e.* to a reduction in the ionization energy.

In support of *Koenig's* assignment of the photoelectron spectrum of **1** we wish to report in Fig. 1 the spectrum of dibenzo-*p*-quinodimethane **6** [9] obtained by pyrolysis at approx. 200° from [2.2] (9,10)anthracenophane **7** [10]:



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Within the range from 8 to 10 eV the photoelectron spectrum of **6** consists of four bands (labelled ① to ④), with relativ intensities of approximately 1:1:1:1. Whereas band ① is well detached, ② overlaps partially with the double band (③, ④) the latter corresponding obviously to two transitions of closely similar ionization energies.

The interpretation of the spectrum is rather straightforward if one applies the LCBO scheme described above. To do so, we use as localized basis orbitals the π-orbitals $\psi_1 = \pi_a$ and $\psi_2 = \pi_{a'}$, for the exocyclic double bonds and the benzene π-orbitals $\psi_{3(6)} = e_{1g}(A)$, $\psi_{4(7)} = e_{1g}(S)$, $\psi_{5(8)} = a_{2u}$ for the *ortho*-phenylene moieties to the left (right) of the xz-plane. For computational purposes all these orbitals are written in their usual *Hückel* LCAO-approximation *e.g.* for the right side phenylene moiety $\psi_6 = e_{1g}(A) = (\phi_2 + \phi_3 - \phi_{11} - \phi_{12})/2$, $\psi_7 = e_{1g}(S) = (2\phi_1 + \phi_2 - \phi_3 - 2\phi_4 - \phi_{12} + \phi_{11})/\sqrt{12}$ and $\psi_8 = a_{2u} = (\phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_{11} + \phi_{12})/\sqrt{6}$ where A and S refer to the antisymmetric or symmetric behaviour of the orbital relative to a plane parallel to the x,z-axes. The basis energies $A_3 = A_4 = A_6 = A_7 = -9.25$ eV, $A_5 = A_8 = -12.25$ eV of the phenylene groups are taken from the known photoelectron spectroscopic data of benzene [11]. The crossterms $B_{\mu\nu}$ between pairs of individual basis orbitals ψ_μ, ψ_ν are calculated in the usual fashion from the atomic orbital coefficients of the corresponding linear combinations of ψ_μ, ψ_ν using $\beta = 2B_{ab} = -2.43$ eV as a resonance integral between two atomic orbitals connected by an essential single bond. Finally the symmetry allowed 'through-space' interaction parameters $B_{\mu\nu}$ between the π-orbitals ψ_3, ψ_4, ψ_5 of the left-hand side *ortho*-phenylene group of **6** with the π-orbitals, ψ_6, ψ_7, ψ_8 of the right-hand side group have to be adjusted relative to $B_{bb'} = -0.5$ eV used in **1** according to the size of the atomic orbital coefficients of the linear combinations at the inner centres 11, 12, 13, and 14. Thus no parameters have to be adjusted or new ones introduced to account for the π-orbital interaction in the molecule **6**. The following matrix of order 8 is obtained, using the abbreviation $B \equiv B_{ab} = -1.21_5$ eV and $B' \equiv B_{bb'} = -0.5$ eV for the cross terms carried over from **1** (all values in eV):

μ,ν	1	2	3	4	5	6	7	8
1	−10.0	0	$B/\sqrt{2}$	$B/\sqrt{6}$	$B/\sqrt{3}$	$B/\sqrt{2}$	$B/\sqrt{6}$	$B/\sqrt{3}$
2		−10.0	$B/\sqrt{2}$	$-B/\sqrt{6}$	$B/\sqrt{3}$	$B/\sqrt{2}$	$-B/\sqrt{6}$	$B/\sqrt{3}$
3			−9.25	0	0	$B'/2$	0	$B'/\sqrt{6}$
4				−9.25	0	0	$B'/\sqrt{6}$	0
5					−12.25	$B'/\sqrt{6}$	0	$B'/3$
6		symm.				−9.25	0	0
7							−9.25	0
8								−12.25

Diagonalization of the above matrix and application of *Koopmans'* approximation ($-\varepsilon_j = I_{v,j}$) yields (in eV):

State of **6**$^+$	$I_{v,j}$(calc)	$I_{v,j}$(obs)
$^2B_{1u}$	7.87	7.95
$^2B_{2g}$	8.62	8.66
$^2B_{3g}$	8.99	9.1
^2A_u	9.17	
$^2B_{1u}$	10.69	10.7
$^2B_{2g}$	10.71	
$^2B_{3g}$	12.26	?
$^2B_{1u}$	13.20	?

The almost perfect agreement between observed ($I_{v,j}$(obs)) and calculated ($I_{v,j}$(calc)) vertical ionization energies leaves hardly any doubt that the proposed assignment is the correct one (see Fig. 1). Thus our results fully confirm the original interpretation of the photoelectron spectrum of **1** due to *Koenig et al.* [1].

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