

## CONJUGATED RADICALS. XVIII.\*

PHOTOELECTRON SPECTROSCOPY AS A SOURCE  
OF ELECTRONIC SPECTRAL DATA FOR RADICAL CATIONS

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Transition energies in radical cations given by photoelectron and optical spectral data have been interpreted by calculations of the PPP and CNDO type, using the one-electron approach (Koopmans' theorem) and the limited configuration interaction treatment based on the open shell SCF MO's. Twelve simple molecules containing 2–12 $\pi$  electrons have been studied. The one-electron MO approach has been examined with regard to its correspondence to the configuration interaction treatment of electronic spectra of radical cations. The limits of this correspondence have been ascertained.

Published electronic spectra are rarer for radical cations than for radical anions, presumably because of preparative problems; there is no method for preparing radical cations as general as, *e.g.*, the alkali metal reduction method for radical anions. Oxidation by Lewis acids is suitable for many systems but is often complicated by competitive  $\sigma$ -bond complex formation<sup>1</sup>. Although the possibilities of electrochemical oxidation have not yet been fully exploited, this method is mostly restricted to fairly large conjugated systems. The  $\gamma$ -irradiation technique in rigid glasses<sup>2</sup> appears to be more useful, but in all of these methods, spectral measurements are often complicated by the presence of dimers or parent neutral compounds. Photoelectron spectroscopy (PES), which is free of these shortcomings, offers excellent possibilities. Here the energy difference between the first and  $n$ -th electron energy peak corresponds to the energy difference between the ground doublet state of the radical cation (formed by ionization of the parent system) and its ( $n-1$ )-th excited doublet state. Of course, one cannot expect complete agreement between the photoelectron and optical spectral data, because the former are measured at a very low pressure in the gas phase whereas the latter are usually measured in solution or a rigid glass. Solvent effect differences are therefore to be expected. Another source of differences is the fact that with the photoelectron and electronic spectra of complex molecules, the 0–0 transitions usually are not available; with photoelectron spectra the transitions are vertical with respect to the equilibrium ground state geometry of the parent closed shell molecule, whereas in electronic spectra the transitions are vertical with respect to the equilibrium ground state geometry of the radical cation. In spite of these differences, the correspondence between the two spectra is remarkably good, and photoelectron spectroscopy thus provides very accurate estimations of transition energies in radical cations<sup>3–5</sup>.

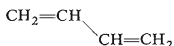
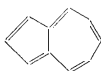
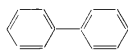
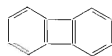
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The present study has been undertaken with a twofold objective: on the one hand, to compare the transition energies given by the photoelectron and electronic spectra with the results of open shell MO calculations; on the other, to examine the limits of a correspondence between the usual one-electron MO approach to the photoelectron spectra and the configuration interaction treatments on optical spectra of radicals. The importance of configuration interaction in interpretations of photoelectron spectra has been pointed out by Lorquet and Desouter<sup>6</sup>.

## METHODS

### Compounds Studied and Treatment of Experimental Data

The choice of the compounds studied was made from the view-points of availability of photoelectron and electronic spectral data and of feasibility of MO calculations by standard semiempirical methods, with the aim of having a model set of compounds covering various structural types. Compromising among these requirements, we have selected systems *I–XII*.

*I**II**III**IV**V**VI**VII**VIII**IX**X**XI**XII*

Energies of excited doublet states have been determined from vertical ionization potentials given by photoelectron spectral data<sup>7–9</sup>: the difference between the *n*-th and the first ionization potentials gives the energy of the (*n*–1)-th excited doublet state of the radical cation. The values of ionization potentials were read from the reported spectra unless they were presented in original publications. From published optical spectra of radical cations, the transition energies were read at positions of the strongest absorption maxima. As an example we present in Fig. 1 the treatment of data for quinoline. With some systems the correspondence between photoelectron and electronic spectra is not unambiguous. In such cases the assignment has been based on semiempirical calculations. In Fig. 2 we present the treatment for quinoline as an example.

## Calculations

We made use of two theoretical approaches. The first is based on the Koopmans' theorem predicting the transition energies in the radical cation by means of a closed shell calculation on the parent system: the energy differences between the highest occupied and lower orbitals are considered as doublet-doublet transition energies in the radical cation. In the second approach, the transition energies of the radical cation have been calculated directly by the open shell treatment using the SCF procedure of Longuet-Higgins and Pople<sup>11</sup> (LHP) followed by configuration interaction (CI) among the singly excited states<sup>12</sup>. The CI basis has been restricted by truncation of the MO set to the four highest doubly occupied orbitals, the singly occupied orbital, and the four lowest unoccupied orbitals. The  $\pi$  electron calculations were of the standard PPP type, evaluating the two-centre repulsion integrals by the Mataga-Nishimoto formula and using the following parameters:  $I_C = 11.22$  eV;  $\gamma_{CC} = 10.53$  eV;  $\beta_{CC} = -2.318$  eV;  $I_N = 14.1$  eV;  $\gamma_{NN} = 12.3$  eV;  $\beta_{CN} = -2.318$  eV. The  $\pi$  electronic structure of indene has been considered to be the same as that of styrene. For systems  $V-XII$  (both for neutral hydrocarbons and radical cations), we employed idealized geometries assuming regular rings and all C—C and C—N bonds

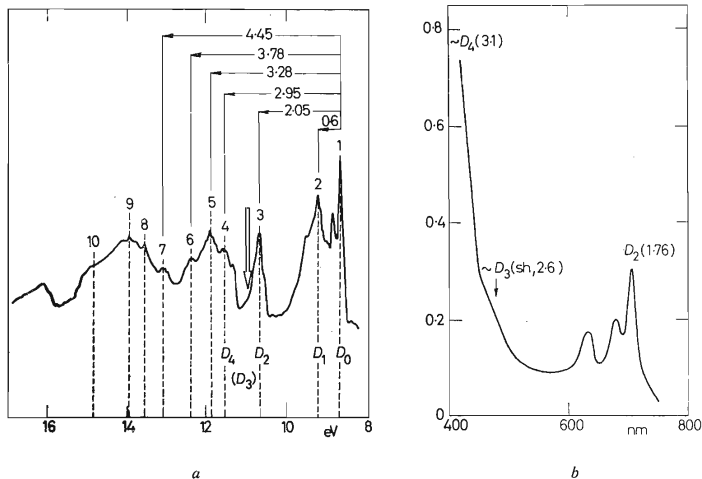


FIG. 1

Determination of Transition Energies in the Quinoline Radical Cation from the Photoelectron Spectrum<sup>9</sup> of Quinoline

Presence of a hidden peak ( $D_3$ ) in the photoelectron spectrum (a) is assumed on the basis of semiempirical calculations and the electronic spectrum<sup>10</sup> of quinoline radical cation (b), the values in parentheses are in eV.

to be 1.40 Å. The geometries used for *I-IV* were inferred from the idealized structures by means of the formula<sup>13</sup>

$$r_{\mu\nu} = 1.515 - \frac{0.180}{1 + 1.05 \left( \frac{1 - \rho_{\mu\nu}}{\rho_{\mu\nu}} \right)},$$

where the  $\rho_{\mu\nu}$  were put equal to HMO bond orders for the neutral hydrocarbons. For *I-IV* and *X* we have also performed the CNDO calculations. We have closely followed the method of Del Bene and Jaffé<sup>14</sup> (DBJ) except for the two-centre repulsion integrals, for which we have used the Mataga-Nishimoto formula rather than that of Pariser and Parr. In closed shell CNDO calculations on ethylene<sup>15</sup> and butadiene<sup>16</sup>, we used experimental geometries. In order to mimic the vertical transitions in photoelectron spectra, the calculations on the ethylene and butadiene radical cations were performed with the geometries of neutral hydrocarbons. With *III*, *IV* and *X* the same geometries were used as those in  $\pi$  electron calculations, assuming the C-H bonds to be 1.1 Å.

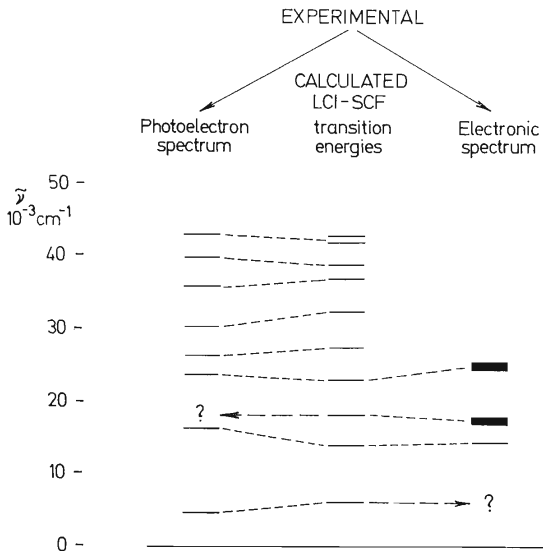


FIG. 2

Transition Energies in the Quinoline Radical Cation

## RESULTS AND DISCUSSION

It is convenient to examine first the extent to which electronic spectral data determined in various ways correspond to each other. The entries in Table I are the transition energies for a series of radical cations determined from photoelectron spectra<sup>7</sup> and by the direct measurements of electronic spectra of radical ions formed upon electron impact<sup>17</sup> or by  $\gamma$ -irradiation<sup>21</sup>. In Tables II and III we compare the observed transition energies of the radical cations derived from I–XII with the results of semi-empirical calculations.

In order to judge the agreement between energies of excited doublet states given by the photoelectron spectra and those measured by the electronic spectra, it is convenient to employ data for small molecules, since their spectra are simple and correspondingly easy to interpret. The entries in Table I show that the agreement is fair.

Hence the photoelectron spectra can be exploited to yield a great deal of information on the electronic spectra of radical cations, provided the parent compounds are neutral closed shell molecules. The most significant merits of PES are the following:

TABLE I  
Comparison of Transition Energies (in  $\text{cm}^{-1} \cdot 10^{-3}$ ) in Radical Cations Given by Photoelectron Spectra (PES)<sup>7</sup> and by Direct Optical Measurements<sup>17</sup>

Parent compound	PES	Electronic spectroscopy	Parent compound	PES	Electronic spectroscopy
HCl	29.05	28.64	CO <sub>2</sub>	30.7	28.5
HBr	29.0	26.57		34.5	34.60
	—	29.23		45.2	45.32
N <sub>2</sub>	10.8	—	OCS	35.0	31.28
	25.7	25.46		39.2	—
	—	(64.62)		54.7	—
CO	23.3 <sup>a</sup>	20.73	CS <sub>2</sub>	21.8	—
	45.7	45.88		35.5	35.23
				49.2	49.07
O <sub>2</sub>	35.5	38.8	Aniline	8.95	—
	47.6	—		22.0	23.3 <sup>c</sup>
	64.6	—			
Cl <sub>2</sub>	21.1 <sup>b</sup>	20.70	Phenol	5.65	—
	35.8 <sup>b</sup>	—		22.9	24.4 <sup>d</sup>
				25.9	26.1 <sup>d</sup>
N <sub>2</sub> O	28.2	28.16		31.5	—
	43.1	—			
	58.2	58.02			

<sup>a</sup> Adiabatic potential: 20 300  $\text{cm}^{-1}$ ; <sup>b</sup> taken from ref.<sup>18</sup>; <sup>c</sup> taken from ref.<sup>19</sup>; <sup>d</sup> average value, ref.<sup>20</sup>.

1) feasibility of measurements; 2) the general applicability permitting data to be obtained even for radical cations difficultly accessible by present methods of radical generation; 3) the possibility of obtaining data for low-lying doublet states hard to measure by the standard technique of electronic spectroscopy in the near infrared region. In general the published electronic spectral data are rather fragmentary in comparison with the photoelectron spectral data. On the other hand, the electronic spectrum of the radical cation, precisely measured over a broad range of wavelengths, can facilitate analysis of the photoelectron spectrum. Thus it is not surprising that with the radical cations derived from *I–XII*, the semiempirical calculations reproduce the transition energies given by PES with an accuracy comparable to that found in electronic spectral data treatments. The first two to four bands in photoelectron spectra can generally be assigned to individual doublet states, but the next bands are usually more complex.

Ethylene gives the poorest agreement between theory and experiment<sup>7</sup> for the entire series *I–XII*, in particular for the two transitions of lowest energy. In the electronic spectra of polyalkyl substituted ethylene radical cations ( $\gamma$ -irradiation<sup>20</sup>), the first band is located in the region 13000–17000  $\text{cm}^{-1}$ . On comparing the  $\pi$  electronic and CNDO calculations on the butadiene radical cation, we assigned the transition energy<sup>7</sup> at 34100  $\text{cm}^{-1}$  to a  $\sigma - \pi$  electron promotion. The absorption band observed at 8000  $\text{cm}^{-1}$  upon the  $\gamma$ -irradiation of butadiene<sup>3,22</sup> has been previously assigned to the butadiene dimer cation radical, both on experimental<sup>3</sup>, and theoretical grounds<sup>28,29</sup>. The transition energies<sup>8</sup> in the radical cations derived from *III* and *IV* are reproduced well by the theory, the agreement being slightly better for *III*. For transition energies in the indene radical cation up to 30000  $\text{cm}^{-1}$ , there is a clear one-to-one correspondence among the photoelectron spectral data for indene<sup>9</sup>, observed transition energies for the styrene radical cation<sup>23</sup>, and the results of the calculation for the model styrene-like  $\pi$  electronic system of the indene radical cation. The nature of higher states is more complex; probably electron transitions related to  $\sigma$  MO's also fall into this region. Fair agreement has also been found for radical cations derived from hydrocarbons *VI–IX*. According to Turner<sup>7</sup> there are "strong grounds for believing that the first five ionization potentials of naphthalene relate to five occupied  $\pi$  orbitals of the molecule". This statement is based on an empirical relationship between the observed ionization potentials and HMO energies of the highest occupied MO's: the correlation predicts five bands below 13.2 eV, in agreement with experiment. Our semiempirical calculations support this assignment but show that only the first three bands in the photoelectron spectrum can be related to ionizations from individual occupied  $\pi$  orbitals. The bands lying in the higher energy region of the photoelectron spectrum are predicted to be more complex and should therefore be considered as superimpositions of several bands, as anticipated by Turner. Optical spectral data<sup>21,23,25,27</sup> for the radical cations derived from *VI–IX* are in fair agreement with those given by PES<sup>7,9,26</sup>; the sole discrepancy concerns

TABLE II  
Comparison of Observed and Calculated Transition Energies in Radical Cations Derived from I-IV and X

PES <sup>a</sup>	PPP-LHP <sup>bc</sup>			LCI-DBI-LHP <sup>bd</sup>			$\epsilon(\text{HOMO}) - \epsilon(0)^f$	DBJ
	$\bar{\nu}$	$\log f$	main configuration	$\bar{\nu}$	$\log f$	main configuration		
Ethylene radical cation								
18.3				27.6	forbidden	A (5-6) $\sigma-\pi$	96.5	26.2
34.0				40.9	-0.64	B (6-7) $\pi-\pi^*$	97.4	
43.6				42.4	forbidden	A (4-6) $\sigma-\pi$	100	39.6
				52.7	forbidden	C <sub><math>\alpha</math></sub> (5-7) $\sigma-\pi^*$	75.0	
				63.2	forbidden	C <sub><math>\alpha</math></sub> (4-7) $\sigma-\pi^*$	75.0	
68.5				64.8	forbidden	A (3-6) $\sigma-\pi$	68.5	75.0
Butadiene radical cation								
18.6 <sup>g</sup>	17.9	-1.85	A (1-2) 57.4	22.7	-1.58	A (10-11) $\pi-\pi$	66.0	25.7
25.4 <sup>g</sup>	28.0	-0.35	B (2-3) 48.0	30.5	-0.32	B (11-12) $\pi-\pi^*$	55.3	
34.0				32.6	forbidden	A (9-11) $\sigma-\pi$	96.0	30.2
38.4	40.4	forbidden	B (2-4) 73.1	38.9	forbidden	B (11-13) $\pi-\pi^*$	80.4	
				39.5	forbidden	A (8-11) $\sigma-\pi$	97.4	36.8
				47.0	-3.46	A (7-11) $\sigma-\pi$	94.0	43.9
Bismethylenecyclobutene radical cation								
5.2	5.3	-2.13	A (2-3) 93.1	8.0	-1.91	A (14-15) $\pi-\pi$	88.8	6.2
	17.4	-1.03	B (3-4) 76.4	21.5	-0.93	B (15-16) $\pi-\pi^*$	75.8	
21.8	20.2	-2.82	B (3-5) 47.6	23.5	-2.05	B (15-17) $\pi-\pi^*$	56.9	
				28.3	forbidden	A (12-15) $\sigma-\pi$	98.5	24.7
				28.8	-3.09	A (13-15) $\sigma-\pi$	99.1	25.9
28.2	30.4	-2.67	C <sub><math>\alpha</math></sub> (2-4) 43.7	37.0	-1.98	B (15-18) $\pi-\pi^*$	43.2	39.4 <sup>h</sup>
36.3	38.1	-1.99	C <sub><math>\beta</math></sub> (2-5) 54.8	38.8	-1.46	C <sub><math>\alpha</math></sub> (14-16) $\pi-\pi^*$	65.3	
42.7	41.8	-0.20	A (1-3) 42.1	43.9	-2.19	C <sub><math>\alpha</math></sub> (12-16) $\sigma-\pi^*$	70.8	
	43.7	-0.25	C <sub><math>\alpha</math></sub> (2-5) 95.5	45.9	forbidden	C <sub><math>\alpha</math></sub> (13-16) $\sigma-\pi^*$	74.7	
50.8	49.9	-0.51	C <sub><math>\beta</math></sub> (2-4) 46.3	48.4	-0.31	C <sub><math>\alpha</math></sub> (14-17) $\pi-\pi^*$	95.1	

## Fulvene radical cation

8.0	10.0	-1.86	A (2-3) 93.1	13.0	-1.70	A (14-15) $\pi-\pi$	90.2	8.5	7.6
	18.4	-2.10	C <sub><math>\beta</math></sub> (2-4) 84.0	23.3	-1.84	B (15-16) $\pi-\pi^*$	77.9		
28.6	20.8	-2.53	B (3-4) 77.3	25.4	-2.18	C <sub><math>\beta</math></sub> (14-16) $\pi-\pi^*$	76.7		
				29.3	forbidden	C <sub><math>\alpha</math></sub> (13-16) $\sigma-\pi^*$	70.1		
				33.1	forbidden	C <sub><math>\beta</math></sub> (13-16) $\sigma-\pi^*$	57.9		21.9
34.3	35.1	-1.04	A (1-3) 72.8	35.6	-3.04	A (13-15) $\sigma-\pi$	99.4	32.8	
				36.6	-1.28	B (15-17) $\pi-\pi^*$	59.7		
				39.8	forbidden	A (12-15) $\sigma-\pi$	94.0		37.8
40.7	35.8	-0.20	C <sub><math>\alpha</math></sub> (2-4) 83.7	41.6	-0.14	C <sub><math>\alpha</math></sub> (14-16) $\pi-\pi^*$	43.8		43.5 <sup>h</sup>
48.8	43.7	-0.54	B (3-5) 40.4	44.7	-1.59	A (10-15) $\pi-\pi$	55.9		45.6
	53.6	-0.87	C <sub><math>\alpha</math></sub> (1-4) 39.9	49.5	-2.26	B (15-18) $\pi-\pi^*$	65.5		

## Pyridine radical cation

6.0	5.0	-3.08	A (2-3) 96.1	7.6	-3.49	A (14-15) $\pi-\pi$	95.9	4.5	3.0
20.3				15.5	forbidden	A (13-15) $\pi-\pi$	98.8		9.9
23.0 <sup>f</sup>	21.3	-1.63	A (1-3) 76.5	28.3	-2.31	A (11-15) $\pi-\pi$	57.6	26.2	25.0
27.6				30.6	-4.46	A (12-15) $\sigma-\pi$	99.4		35.6
32.5	31.8	-1.48	B (3-5) 45.2	31.2	-1.47	B (15-17) $\pi-\pi^*$	47.1		
				33.3	-2.36	C <sub><math>\alpha</math></sub> (13-16) $n-\pi^*$	66.6		
37.5	41.6	-1.81	B (3-4) 53.6	41.4	-2.35	B (15-16) $\pi-\pi^*$	48.4		37.4 <sup>h</sup>
				42.8	forbidden	C <sub><math>\alpha</math></sub> (13-17) $n-\pi^*$	75.0		
46.4	45.5	-0.84	B (3-5) 49.3	45.5	-0.82	C <sub><math>\alpha</math></sub> (14-16) $\pi-\pi^*$	50.5		46.8 <sup>h</sup>
				47.6	-2.82	C <sub><math>\beta</math></sub> (13-16) $n-\pi^*$	67.9		
	53.6	-0.11	C <sub><math>\beta</math></sub> (2-5) 29.6	54.8	-1.36	B (15-18) $\pi-\pi^*$	80.4		
	55.1	-0.32	C <sub><math>\alpha</math></sub> (2-4) 86.5	55.8	-0.34	C <sub><math>\alpha</math></sub> (14-16) $\pi-\pi^*$	90.6		
	57.1	-1.55	B (3-6) 56.2	57.6	-0.05	A (11-15) $\pi-\pi$	35.9		
				57.9	-3.96	C <sub><math>\alpha</math></sub> (12-17) $\sigma-\pi^*$	74.4		
59.3	59.6	-1.15	C <sub><math>\beta</math></sub> (2-6) 48.1	58.1	forbidden	C <sub><math>\alpha</math></sub> (12-16) $\sigma-\pi^*$	73.3		
				59.4	-1.60	C <sub><math>\beta</math></sub> (14-18) $\pi-\pi^*$	66.1		60.4 <sup>h</sup>

<sup>a</sup> Transition energies given by the photoelectron spectra (in  $\text{cm}^{-1} \cdot 10^{-3}$ ); for references see text. <sup>b</sup> Calculated transition energies, logarithms of oscillator strengths, and main configurations in upper states (weights in %); for definitions of the A, B, C <sub>$\alpha$</sub> , and C <sub>$\beta$</sub>  types of configurations see ref. 12 and text. <sup>c</sup>  $\pi$  Electron open shell calculations on radical cations. <sup>d</sup> CNDO open shell calculations on radical cations. <sup>e</sup> Differences in closed shell SCF orbital energies for the highest occupied and lower MO's in parent compounds. <sup>f</sup> The electronic spectral data are  $2.17 \cdot 10^5$  and  $2.5 \cdot 10^5 \text{ cm}^{-1}$ . <sup>g</sup> This pure electronic transition has no counterpart in the LCI open shell calculation. <sup>h</sup> The electronic spectrum <sup>10</sup> exhibits a band at  $23\,300\text{--}26\,400 \text{ cm}^{-1}$  with the maximum at about  $25\,000 \text{ cm}^{-1}$ .



TABLE III

Comparison of Observed and Calculated Transition Energies in Radical Cations Derived from *V*—*IX*, *XI* and *XII*

PES <sup>a</sup>	Electronic spectra	PPP—LHP <sup>b</sup>			$\epsilon(\text{HOMO}) - \epsilon(i)^c$
		$\tilde{\nu}$	$\log f$	main configuration	
Indene radical cation <sup>d</sup>					
6.6		6.7	-3.25	A (3-4) 90.9	7.2
17.4	15.7	15.4	-1.10	A (2-4) 78.6	17.0
24.0	24.4	23.9	-0.76	B (4-5) 39.9	
27.8	28.6	28.3	-0.69	A (1-4) 56.6	33.0
		34.4	-1.68	B (4-7) 43.5	
38.5		36.7	-0.92	C <sub><math>\alpha</math></sub> (3-5) 67.3	
		40.2	-1.32	B (4-6) 61.6	
44.1		46.8	-1.85	C <sub><math>\beta</math></sub> (3-6) 33.1	
53.0		7 transitions between 50.4 and 59.7			
64.3		65.3	-1.35	C <sub><math>\alpha</math></sub> (1-5) 88.2	
Naphthalene radical cation					
5.6		7.7	forbidden	A (4-5) 93.8	7.9
14.9	14.2 <sup>e</sup>	14.4	-1.04	A (3-5) 91.0	16.1
		19.2	-2.22	A (2-5) 59.5	23.7
23.0	22-23 <sup>e</sup>	22.7	-0.94	B (5-6) 44.2	
		28.5	forbidden	B (5-8) 37.7	
33.5		34.4	-0.71	C <sub><math>\alpha</math></sub> (4-6) 51.3	
		37.3	-0.44	C <sub><math>\beta</math></sub> (4-6) 46.2	
		39.7	forbidden	A (1-5) 43.1	38.3
		42.3	forbidden	B (5-9) 47.0	
43.5		43.9	-1.00	C <sub><math>\beta</math></sub> (4-7) 66.2	
		46.3	forbidden	C <sub><math>\alpha</math></sub> (4-8) 38.5	
48.2		48.0	forbidden	C <sub><math>\alpha</math></sub> (3-6) 94.9	
		49.3	-0.01	C <sub><math>\beta</math></sub> (4-6) 41.8	
		52.3	-0.44	C <sub><math>\alpha</math></sub> (4-7) 91.7	
Azulene radical cation <sup>f</sup>					
8.5	~9	9.1	-2.88	A (4-5) 92.1	8.8
20.7	15; ~19	19.8	-1.99	B (5-7) 41.7	24.5 <sup>g</sup>
		21.5	-3.06	B (5-6) 79.5	
		24.2	-1.56	C <sub><math>\beta</math></sub> (4-6) 53.8	
26.9	~26	26.1	-2.03	A (2-5) 47.9	30.3
		30.5	-4.07	C <sub><math>\alpha</math></sub> (4-6) 31.7	
		33.6	-2.33	C <sub><math>\beta</math></sub> (3-6) 40.4	

TABLE III  
(continued)

PES <sup>a</sup>	Electronic spectra	PPP—LHP <sup>b</sup>			$\epsilon(\text{HOMO}) - \epsilon(i)^c$
		$\bar{\nu}$	$\log f$	main configuration	
Diphenyl radical cation <sup>h</sup>					
7.1		7.5	forbidden	A (5-6) 95.8	7.1
		7.7	-2.72	A (4-6) 95.5	7.5
12.1	14.1	14.1	-0.60	A (3-6) 91.0	14.1
22.8	~ 25	23.3	forbidden	A (2-6) 70.2	28.3
31.5	~ 26.3	27.2	-0.50	B (6-7) 63.9	
		35.5	forbidden	B (6-10) 30.2	
Diphenylene radical cation <sup>i</sup>					
9.4	(6.6)	8.9	-2.23	A (5-6) 95.3	8.7
	16.1	15.7	forbidden	B (3-6) 59.2	
		17.3	forbidden	A (6-7) 55.6	17.1
	(~ 18)	18.3	-0.82	A (4-6) 87.3	19.3
	(25.6)	25.7	forbidden	A (2-6) 62.8	31.0
		27.9	-1.45	C <sub><math>\beta</math></sub> (5-7) 52.5	
		29.1	-0.43	C <sub><math>\alpha</math></sub> (5-7) 51.8	
	(30.8)	32.9	-2.98	B (6-10) 43.5	
		35.5	forbidden	B (6-9) 41.5	
	(37.2)	38.0	forbidden	C <sub><math>\beta</math></sub> (5-8) 70.3	
		39.7	0.15	B (6-8) 34.0	
Quinoline radical cation <sup>j</sup>					
4.8		6.1	-3.63	A (4-5) 93.8	5.6
16.5	14.3	14.3	-1.10	A (3-5) 86.2	16.1
	~ 17.5	18.6	-1.99	A (2-5) 60.2	22.9
23.8	~ 25	23.7	-1.03	B (5-6) 42.1	
26.2		28.5	-1.91	A (1-5) 36.6	37.6
30.2		33.3	-0.39	C <sub><math>\alpha</math></sub> (4-6) 47.8	
35.9		37.7	-1.71	B (5-7) 42.5	
39.9		40.3	-1.82	A (1-5) 32.3	
43.2		42.8	-0.80	B (5-9) 23.1	
		43.8	-0.88	C <sub><math>\beta</math></sub> (4-7) 51.9	
Isoquinoline radical cation <sup>j</sup>					
7.8		8.9	-2.71	A (4-5) 92.5	9.4
15.6	14.2	14.3	-1.03	A (3-5) 90.3	16.1
	21 <sup>k</sup>	20.7	-2.98	B (5-6) 49.1	
24.5	25 <sup>l</sup>	22.6	-0.97	A (2-5) 35.7	25.9

TABLE III  
 (continued)

PES <sup>a</sup>	Electronic spectra	PPP—LHP <sup>b</sup>			$\epsilon(\text{HOMO}) - \epsilon(i)^c$
		$\tilde{\nu}$	$\log f$	main configuration	
26.9		28.9	-3.76	A (1-5) 33.0	
31.9		34.2	-1.89	B (5-7) 54.4	
37.5		37.5	-0.35	C <sub><math>\beta</math></sub> (4-6) 45.0	
		39.5	-1.08	A (1-5) 34.7	38.9
		41.9	-1.74	B (5-9) 47.8	
44.2		44.5	-0.51	C <sub><math>\beta</math></sub> (4-7) 50.7	
		46.3	-1.57	C <sub><math>\alpha</math></sub> (3-6) 30.3	
		47.7	-1.21	C <sub><math>\alpha</math></sub> (3-6) 48.3	
50.6		50.3	-0.20	C <sub><math>\alpha</math></sub> (4-6) 27.0	

<sup>a</sup> Transition energies given by the photoelectron spectra (in  $\text{cm}^{-1} \cdot 10^{-3}$ ), taken from ref.<sup>9</sup> unless otherwise noted; <sup>b</sup> cf. footnotes *b* and *c* in Table II; <sup>c</sup> PPP calculation, cf. footnote *f* in Table II; <sup>d</sup> electronic spectral data and the calculation refer to the styrene radical cation, the former were taken from ref.<sup>21</sup>; <sup>e</sup> taken from ref.<sup>23</sup>; <sup>f</sup> the photoelectron spectral data are taken from ref.<sup>24</sup>, the electronic spectral data for 1,3-di-tert-butylazulene radical cation from ref.<sup>25</sup>; <sup>g</sup> this pure electronic transition has no counterpart in the LCI open shell calculation; <sup>h</sup> electronic spectral data taken from ref.<sup>21</sup>; <sup>i</sup> photoelectron spectral data are taken from ref.<sup>26</sup>, the optical spectral data from ref.<sup>27</sup>, the pairing properties of MO's permit to use the data observed for the radical anion (in parentheses); <sup>j</sup> electronic spectral data taken from ref.<sup>10</sup>; <sup>k</sup> a shoulder; <sup>l</sup> a rough estimate.

the peak at  $15000 \text{ cm}^{-1}$  of the broad band observed in the electrochemical oxidation of 1,3-di-tert-butylazulene<sup>25</sup>. The situation with the three nitrogen analogs (X—XII) can be considered satisfactory. The  $\pi$  electron calculation for X does not account for the transition energies<sup>9</sup> at  $20300$  and  $27600 \text{ cm}^{-1}$ . On the basis of the CNDO calculation we have assigned them to  $n \rightarrow \pi$  and  $\sigma \rightarrow \pi$  transitions (Table II). With XI and XII there is no one-to-one correspondence between the photoelectron<sup>7,9</sup> and optical<sup>10</sup> spectral data, but the "missing" states need not be observable by the respective spectroscopic techniques. This is strongly supported by theory, as seen in Fig. 2 for XI.

Concerning the established correspondence between the transition energies given by PES and those observed in electronic spectra of the radical cations, it may be asked how the one-electron approach (Koopmans' theorem), which has been applied widely and successfully to PES, is compatible with a many-electron approach (open shell LCI calculations) for the analysis of the electronic spectra of radical cations. On theoretical grounds one can expect that the one-electron approach is justifiable provided that: First, the several lowest electronic transitions in the radical cation are of the A-type, *i.e.* from the doubly occupied MO to the singly occupied MO. Second,

the mixing of configurations of the same symmetry must be unimportant, *i.e.* the transitions must be due to rather pure electron promotions. The actual calculations support this statement. By examination of the entries in Tables II and III, it is seen that a fair agreement between the one-electron and many-electron approaches is found only with systems satisfying the two requirements. In general, the many-electron approach should be preferred, since in a region of higher energy the B-type (singly occupied MO  $\rightarrow$  virtual MO) and C-type (doubly occupied MO  $\rightarrow$  virtual MO) transitions predominate over the A-type transitions. On the other hand, it is convenient to arrive at reasonable transition energies for the first and perhaps even for the second band of the radical cation by means of the SCF closed shell calculation on the parent system. Several energy lowest bands in PES can mostly be assigned to individual doublet states, but the next bands are usually rather complex and are in fact superimpositions of several bands. The  $\pi$  electron calculations are superior to the CNDO ones in predictions of  $\pi - \pi$  transitions. The latter indicate, however, that  $\sigma$  electrons should be accounted for in some conjugated systems even in the low-energy spectral region.

## REFERENCES

1. Aalbersberg W. I., Hoijtink G. J., Mackor E. L., Weijland W. P.: *J. Chem. Soc.* 1959, 3055.
2. Hamil W. H. in the book: *Radical Ions* (E. T. Kaiser, L. Kevan, Eds), p. 321. Interscience, New York 1968.
3. Badger B., Brocklehurst B.: *Trans. Faraday Soc.* 65, 2576 (1969).
4. Herzberg G.: *Quart. Rev.* 25, 201 (1971).
5. Dixon R. N., Duxbury G., Horani M., Rostas J.: *Mol. Phys.* 22, 977 (1971).
6. Lorquet J. C., Desouter M.: *Chem. Phys. Letters* 16, 136 (1972).
7. Turner D. W., Baker C., Baker A. D., Brundle C. R.: *Molecular Photoelectron Spectroscopy*. Wiley-Interscience, London 1970.
8. Heilbronner E., Gleiter R., Hopf H., Hornung V., de Meijere A.: *Helv. Chim. Acta* 54, 783 (1971).
9. Eland J. H. D., Danby C. J.: *Z. Naturforsch.* 23a, 355 (1968).
10. David C., Janssen P., Geuskens G.: *Spectrochim. Acta* 27A, 367 (1971).
11. Longuet-Higgins H. C., Pople J. A.: *Proc. Phys. Soc. (London)* A 68, 591 (1955).
12. Zahradnik R., Čárský P.: *J. Phys. Chem.* 74, 1235 (1970).
13. Streitwieser A., jr: *Molecular Orbital Theory for Organic Chemists*, p. 167. Wiley, New York 1961.
14. Del Bene J., Jaffé H. H.: *J. Chem. Phys.* 48, 1807 (1968).
15. *Tables of Interatomic Distances and Configuration in Molecules and Ions* (L. E. Sutton, Ed.). The Chemical Society, London 1958.
16. Kuchitsu K., Fukuyama T., Morino Y.: *J. Mol. Structure* 1, 469 (1968).
17. Herzberg G.: *Molecular Spectra and Molecular Structure*. I. *Spectra of Diatomic Molecules*. Van Nostrand, New York 1959; III. *Electronic Spectra and Electronic Structure of Polyatomic Molecules*. Van Nostrand, New York 1966.
18. Frost D. C., McDowell C. A., Vroom D. A.: *J. Chem. Phys.* 46, 4255 (1967).
19. Shida T., Hamill W. H.: *J. Chem. Phys.* 44, 2369 (1966).
20. Habersbergerová A., Janovský I., Teplý J.: *Radiation Res. Rev.* 1, 109 (1968).

21. Shida T., Hamill W. H.: *J. Chem. Phys.* **44**, 4372 (1966).
22. Shida T., Hamill W. H.: *J. Am. Chem. Soc.* **88**, 5371 (1966).
23. Shida T., Hamill W. H.: *J. Chem. Phys.* **44**, 2369 (1966).
24. Dewar M. J. S., Haselbach E., Worley S. D.: *Proc. Roy. Soc. (London)* **A315**, 431 (1970).
25. Nykl I., Fojtik A., Hobza P., Čársky P., Zahradník R., Shida T.: *This Journal*, in press.
26. Eland J. H. D.: *Internat. J. Mass. Spectr. Ion Phys.* **2**, 471 (1969).
27. Hush N. S., Rowlands J. R.: *Mol. Phys.* **6**, 317 (1963).
28. Badger B., Brocklehurst B.: *Trans. Faraday Soc.* **66**, 2939 (1970).
29. Čársky P., Zahradník R.: *Theoret. Chim. Acta* **20**, 343 (1971).

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