58. The Photoelectron Spectrum of [18]Annulene

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Summary

The PE. spectrum of [18]annulene has been measured and correlated with MO-calculations. The experimental ionization energies can only be explained by computing the electronic states of the cation, that is by taking into account the electron correlation and reorganization in the ionic states. The results allow a discussion of the structure of the neutral molecule; they are consistent with a D_{6h} point group of symmetry.

Introduction. - In a recent study on the low-temperature UV./VIS. absorption spectrum of [18]annulene we have reviewed the controversy on the structure of this molecule [1]. A structure of D_{6h} symmetry was proposed on the basis of an X-ray analysis [2], of the UV./VIS. spectrum [3], of NMR. [4], and of thermochemical [5] measurements. On the other hand a structure of D_{3h} symmetry was predicted by different authors on the basis of various calculations [6–12]. The importance of electron correlation in computations of molecular energies and geometries of large annulenes was studied by one of the authors [13] who concluded that cyclic [4n+2]-π-systems with a twofold axis or a plane through a π-center are stabilized by electron correlation. This finding is now supported by recent MNDOC-computations [14] [15].

In this paper we discuss the PE. spectrum of [18]annulene recorded at 150°. CNDO/S-CI-Calculations [16] [17] are performed for the purpose of interpreting the experimental spectrum. The question of the symmetry of the molecule and its cation is rediscussed.

Experimental results. - *PE. Spectrum.* The data were obtained using a *PS-18*-spectrometer from *Perkin-Elmer* (Beaconsfield, England). The calibration was made by introducing small amounts of a mixture of Xe ($^2P_{1/2}$, $^2P_{3/2}$ doublet at 12.130 and 13.436 eV) and Ar ($^2P_{1/2}$, $^2P_{3/2}$ doublet at 15.759 and 15.937 eV) in the target chamber. To avoid oxidation of the [18]annulene the samples were sealed under vacuum in small pyrex ampullas which were opened immediately prior to their introduction into the spectrometer. To get a sufficiently high vapour pressure inside the target chamber the sample holder had

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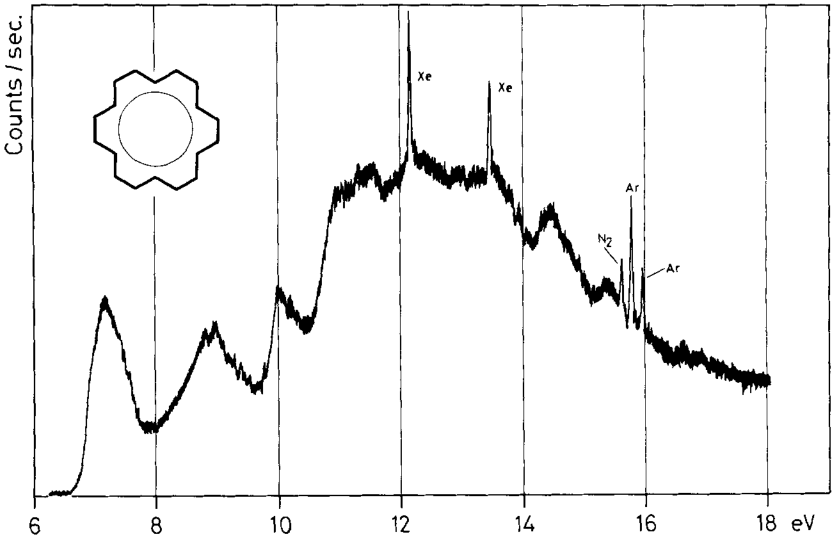

Fig. 1. *Overall PE. spectrum of [18]annulene*

to be heated around 150-155°. This temperature corresponds more precisely to the temperature of the metallic insert holding the pyrex ampulla. The actual sample temperature may be substantially lower than 150°. Since [18]annulene was known to thermally decompose in solution above 100° [5] many experiments were carried out to insure that the spectrum reported in *Figure 1* does not contain features from other compounds. One of the decomposition products of [18]annulene is benzene which has a very characteristic PE. band with vibrational structure at 9.25 eV. This band appears about 1½ h after the introduction of the sample in the spectrometer. *Figure 2* displays rapidly scanned spectra of [18]annulene 1½, 2, 2½ and 3 h after sample introduction. The benzene band grows slowly with time and at least three new bands, centered around 7.4, 8.3 and 9.5 eV appear. These bands arise from other decomposition intermediates or products like the tetracyclic compound or the benzocyclooctatriene [5]. None of these features (and especially the benzene band) are present in the spectrum recorded immediately after the introduction of the sample *(Fig. 1)*; we thus conclude that it corresponds to the actual PE. spectrum of [18]annulene. The experimentally determined ionization potentials (IP). are reported in *Table 1*.

Theoretical results. – *Geometry-optimization calculations.* According to its crystal structure [2], [18]annulene is nearly planar, has delocalized π-bonds but is

Table 1. *Vertical ionization potentials* (IP's, eV)[a]) *of [18]annulene*

Band	IP's
1	7.23[b])
2	8.82, 8.99
3	10.02
4	11.0, 11.5, 12.5, 13.1, 13.5[c])
5	14.42
6	15.34
7	16.8

[a]) Maximum of *Frank-Condon* envelope; average of three determinations, ±0.05 or ±0.1 eV. [b]) Adiabatic IP.: 6.60 eV; the asymmetry on the high energy side may arise from a *Jahn-Teller* splitting (~0.25 eV). [c]) Very broad band with diffuse maxima.

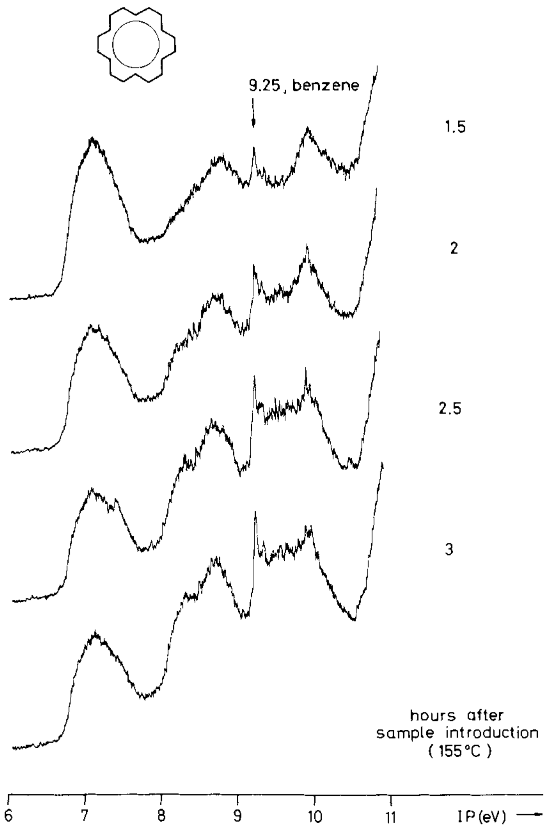

Fig. 2. *Thermal decomposition of [18]annulene as observed by PE. spectroscopy*

slightly distorted from an ideal D_{6h} symmetry: it belongs to the point group C_i. Neglecting the out-of-plane deviations, a structure belonging to C_{2h} symmetry (*Fig. 2* in [1]) can be obtained. Moreover, only small corrections are necessary to idealize this latter structure so that it belongs to the D_{6h} point group of symmetry (*Fig. 3* in [1]). We have performed geometry-optimization calculations using a modified program (OPTMO90)[2]) from *Komornicki & McIver* [18]; the results of this MINDO/2-optimized structure, belonging to the D_{3h} point group of symmetry, are summarized in *Figure 4* in [1]. It is very similar to the structures found by *Allinger et al.* [7] and *Dewar et al.* [8]. For the cation ground state we propose the OPTMO90-[18]optimized dication structure, whereby the D_{3h}-like C_{2v} geometry was found to be more stable than the D_{6h}-like C_{2h} structure.

CNDO/S-CI-Calculations [16]. The theoretical interpretation of the PE. spectrum was attempted, in a first step, by use of *Koopmans'* theorem. The ionization

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[2]) OPTMO90, being suitable to treat large molecules, is a strongly modified version of the original program.

potentials were compared with the orbital energies computed by the program CNDUV99 [17] for both D_{3h} and D_{6h} symmetries *(Table 2)*. The results are not satisfying; especially the second IP. at 8.82, (8.99) eV is not reproduced by this simple approach. We therefore computed the electronic states of the cation by using the D_{3h}-like C_{2v}- and D_{6h}-like C_{2h}-structures and the program ONDUV99 [19] *(Table 2)*. The second and third IP.'s appear to be due to the A_2, B_1 or B_g, A_u states of the C_{2v} and C_{2h} structures, respectively, which cannot be simply related to one single molecular orbital. In *Table 2* the percentages of the one-hole configurations in the computed electronic states of the cation are also given. The first PE. band corresponds to one nearly pure electronic configuration, whereas the second and third bands are due to strongly mixed states. The fourth very broad band with diffuse maxima at 11.0, 11.5, 12.1 and 13.1 eV arises from at least three rather pure (B_2, B_2, A_1 or B_u, B_u, A_g) states and from many mixed states. From the data listed in *Table 2*, it is evident that the experimental differences of ionization energies are better reproduced if a D_{3h}-like structure is assigned to the cation. Our computational

Table 2. *CNDO/S-orbital energies of [18]annulene* and CNDO/S-CI-*computed states of its cation* (eV)

Nr	CNDO/S-Orbitals								CNDO/S-CI-States						Exp.
	Energy	'D_{3h}'	C_{2v}	Type	Energy	'D_{6h}'	C_{2h}	Type	Energy	C_{2v}	One-hole %	Energy	C_{2h}	One-hole %	
1	7.91	e''	b_1	π	7.26	e_{2u}	a_u	π	7.85	B_1	98	7.74	A_u	96	7.23
	8.00		a_2	π	7.30		a_u	π	8.44	A_2	87	7.94	A_u	94	
2									9.75	A_2	2	9.19	B_g	2	8.82
									9.91	B_1	38	9.31	B_g	6	8.99
									9.96	A_2	44	9.46	B_g	31	
	10.16	a_1''	a_2	π	9.91	b_{2g}	b_g	π				9.61	B_g	31	
3	10.21	a_2''	b_1	π	10.11	b_{1g}	b_g	π	10.70	B_1	11	10.89	A_u	20	10.02
									11.05	A_2	50	10.96	A_u	18	
									11.18	B_1	46	11.29	B_g	17	
												11.44	B_g	57	
												11.53	B_g	39	
4	11.30	a_2'	b_2	σ	11.98	b_{2u}	b_u	σ	11.49	A_2	12	11.74	A_u	2	11.00
									11.55	B_1	22	11.78	A_u	3	
									11.60	B_2	99	11.81	B_g	1	11.50
									11.64	A_2	18	12.50	A_u	0	
									11.97	B_1	0	12.52	A_u	0	
	11.74	e'	a_1	σ	12.15	e_{2u}	a_u	π	12.21	B_2	88	12.67	B_g	3	12.50
	11.80		b_2	σ	12.26		a_u	π	12.47	A_1	95	12.83	B_u	100	
									12.56	A_2	8	12.85	A_u	0	
									12.63	B_1	17	12.85	B_g	0	
									13.06	A_2	47	12.95	A_u	2	13.10
	12.27	e''	a_2	π	12.27	e_{2g}	a_g	σ	13.11	B_1	51	13.12	B_u	99	
	12.29		b_1	π	12.32		b_u	σ	13.14	B_1	2	13.13	A_u	44	
									13.17	A_2	15	13.15	A_u	39	
									13.22	A_2	2	13.19	A_g	99	
									13.42	A_2	6				
									13.43	B_1	1				
									13.56	A_1	0				

Table 3. *MNDO- [20] and MNDOC- [15] computed states of the cation of [18]annulene*

D_{6h}	MNDO	MNDOC	D_{3h}	MNDO	MNDOC
E_{2u}	6.99	7.15	E''	7.94	8.04
B_{2g}	8.64	9.07	A_2''	9.29	9.62
B_{1g}	8.73	9.14	A_1''	9.36	9.69
E_{2u}	10.24	10.78	E''	10.61	11.15

results in *Table 3* may be compared with those of the MNDO- [20] and MNDOC- [15] calculations of *Thiel* [21].

Conclusions. - On the basis of many experimental facts and their interpretation [2-5] we are confident that [18]annulene has a structure with D_{6h}-symmetry. The computational preference for a D_{3h}-symmetry is almost certainly due to the neglect of the correlation energy. On the other hand it is rather sure that the cation of this molecule (no(4n+2)-system, where the correlation is important) has localized π-bonds and is best described by a distorted D_{3h}-structure, often proposed for the neutral compound.

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