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Molecular Orbital Calculations for Tetracene Monopositive Ion

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Molecular orbital calculations on the energy levels of the monopositive ion of tetracene has produced the same result as for the mononegative ion of tetracene, in accordance with the theoretical prediction that the electronic spectra of both the tetracene ions should be identical.

Certain aromatic hydrocarbons (M), when dissolved in strong inorganic acids, are converted to their monopositive ions (M^+) and proton complexes (MH^+). The concentration of M, in comparison with the concentration of M^+ and MH^+ in solution is negligible. The ratio M^+/MH^+ depends, on the proton activity and the oxidising power of the acid. The ratio M^+/MH^+ is very large for tetracene (T), and this means that T can be readily oxidised to its monopositive ion which is not true, for example, for anthracene (anthracene mainly forms a proton complex), the difference in the redox potentials of tetracene and anthracene might be reason for such different behaviour. The electronic spectrum of tetracene monopositive ion (T^+) was obtained by Aalbersberg, Hoijtink, Mackor and Weijland[1]. The spectrum of T in H_2SO_4 (conc.) or in $CF_3 - CO_2H + BF_3$, H_2O (in presence of oxygen) is almost identical with the spectrum of tetracene mononegative ion (T^-). The electronic spectrum of T obtained by alkali metal reduction has been measured by a number of workers, but for comparison we shall take the most recent experimental data reported by Buschow and Hoijtink[2]. The experimental data are given in Table 1.

The Hückel theory[3] predicts that the absorption spectra of an alternant aromatic hydrocarbon cation and anion should be identical: this follows from the pairing properties of the Hückel molecular orbitals of alternants. It has been pointed out by several authors that the more exact theories (the electron interaction terms included in the Hamiltonian) would reach the same conclusion**. The tetracene ions are very good examples to test such a prediction.

We have carried out MO calculations to determine the energy levels for T^+. The following MO methods have been used: Hückel (HMO) theory (with the value for $\beta = -3.3$ eV), Pariser-Parr (P) method[5] and the simplified version of the P-method proposed by Longuet-Higgins and Salem[6]***. The carbon skele-

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** The most complete theory has been given by McLachlan[4].

*** The simplified P-method was applied by Weltin, Weber and Heilbronner[7] to the neutral aromatic hydrocarbons, by Favini, Vandoni and Simonetta[8] to the aza aromatic hydrocarbons, and by Hinchliffe, Murrell and Trinajstić[9] to the mono- and dinegative ions of alternant aromatic hydrocarbons, giving always the best agreement with experiment.

TABLE 1

Experimental Data

All results are in eV. The energies quoted refer either to maxima or shoulders. Symmetry assignements of bands for the alternant hydrocarbon anions have been proposed in ref. 9.

Symmetry	T^+						T^-	
	Ref. 1						Ref. 2	
	HF (anhydr.)		H_2SO_4 (conc.)		$CF_3 — CO_2H + BF_3, H_2O$		Alkali metal reduction	
	eV	$\varepsilon/\nu \cdot 10$	eV	$\varepsilon/\nu \cdot 10$	eV	$\varepsilon/\nu \cdot 10$	eV	$\varepsilon/\nu \cdot 10$
B_{3g}			1.32	1.0			1.45	1.3
B_{2u}			1.44	15.7	1.44	10.0	1.57	18.0
			1.54	5.7			1.60	7.3
			1.64	7.0	1.64	4.5	1.73	8.7
			1.91	2.9			1.98	3.3
	2.06	4.0						
	2.40	3.3						
	2.85	21.3	2.85	1.4	2.85	0.5		
B_{2u}			3.10	13.7	3.20	13.0	3.10	19.3
			3.30	5.0	3.30	4.6	3.26	6.0
B_{2u}			3.59	16.2	3.60	6.7	3.47	23.3
	4.01	2.0						
	4.26	2.0						
			4.53	35.0			4.34	36.0
B_{2u}	5.06	4.7						

ton of tetracene with the numbering of the carbon atoms is shown in Fig. 1. The symmetries of some one-electron transitions for T^+ are shown in Fig. 2. The calculated transition energies are given in Table 2, and calculated oscillator strengths are in Table 3. The HMO π-electron densities and the π-bond orders are given in Table 4. The results for the transition energies have been compared with those in Ref. 9 for T^-, and it is found that *all* three MO methods give identical numerical results for T^+ and T^- (we restricted configuration interaction in the same way as was done in Ref. 9).

TABLE 2

Calculated Transition Energies. All calculated energies are in eV.

Symmetry	HMO	P-Method	Simplified P-Method
B_{3g}	2.3	1.6	1.6
B_{2u}	1.6	1.6	1.4
B_{1u}	2.0	2.1	1.8
B_{1u}	3.3	3.5	2.9
B_{2u}	3.9	3.8	3.3
B_{2u}	4.3	4.2	3.5
B_{2u}	4.3	6.1	4.0

However, the experimental spectrum of T^+ differ slightly from that of T^- (see Table 1). There is a band at 2.85 eV in the spectrum of T^+, which is not observed in that of T^-. The intensity of this band and the entire spectrum of

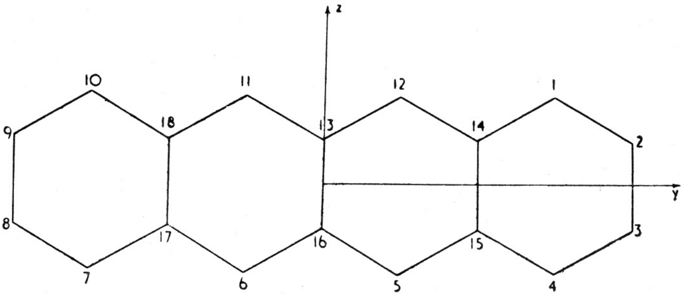

Fig. 1. Carbon skeleton of tetracene.

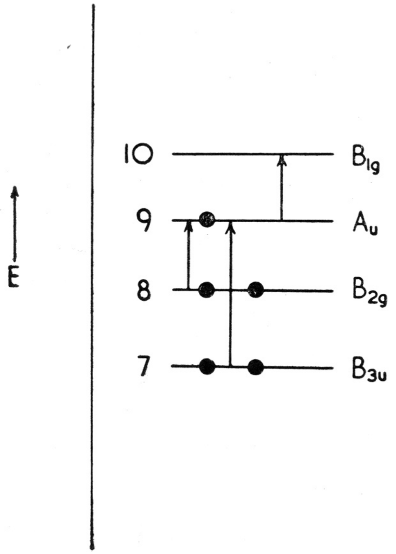

Fig. 2. Some of one-electron transitions for tetracene monopositive ion.

TABLE 3

Calculated Oscillator Strengths

	HMO	P-Method
B_{3g}	0	0
B_{2u}	0.21	0.11
B_{1u}	0.15	0.02
B_{1u}	0.19	0.42
B_{2u}	0.40	0.20
B_{2u}	0.40	1.20

T^+ vary with the type of acid used to prepare it. Because of this, it is likely that the strong band at 2.85 eV, when T is dissolved in HF(anhydr.) is due only to the formation of TH^+. On the other hand one can also attribute the weak band at 2.85 eV to a very small amount of TH^+, which might be still present when T is dissolved in H_2SO_4 (conc.) or in $CF_3 - CO_2H + BF_3, H_2O$. The interesting point is that one of our calculations, obtained by the simplified

P-method, has predicted the second B_{1u} band at 2.9 eV with low intensity. There is also a slight difference in the positions of the bands of T^+ and T^-, which may be due to differences in the methods of preparation or to solvent effects.

TABLE 4

HMO π-Electron Densities and π-Bond Orders of T^+ and T^-.
The average π-bond order for T^+ is 0.580 and is only slightly different from the π-bond order for T (0.593) and this allowed us to use the same parameters as those for the neutral molecule.

Atom	π-Electron Density	
	T^+	T^-
1	0.944	1.056
2	0.966	1.034
12	0.853	1.147
13	1.000	1.000
14	0.987	1.013

Bond	π-Bond Order
	T^+ and T^-
1— 2	0.698
1—14	0.557
12—13	0.584
12—14	0.575
14—15	0.488
13—16	0.458
2— 3	0.614

Finally, the HMO π-bond orders of both T^+ and T^- are identical, but the HMO charge distribution in T^+ tends to lie towards the centre of molecule, while in T^- it tends to lie away from the centre.

The numerical computations have been performed on the ICT computer at University of Sheffield.

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IZVOD

Molekularno-orbitalni račun za tetracen monopozitivan ion

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Molekularno-orbitalni (MO) račun energetskih nivoa monopozitivnog iona tetracena je dao isti rezultat kao i za mononegativni ion tetracena, što je u skladu sa teorijom, da elektronski spektri obadva iona tetracena treba da su identični.

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