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PHOTOELECTRON SPECTRUM (HeI) OF 9-METHYLANTHRACENE

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A photoelectron spectrum of 9-methylanthracene, with first five π bands located at 7.25, 8.43, 9.07, 9.87, and 10.30 eV, is presented. Assignments of the bands based on CNDO and INDO calculations are given. In comparison with the spectrum of anthracene, the effects of the methyl group in 9-methylanthracene on the photoelectron spectrum are explained well by the MO calculations.

Recently, the photoelectron spectra of the condensed polycyclic aromatic hydrocarbons have been reported by several workers.[1 - 4] It is probable that the substituents introduced into these highly symmetric hydrocarbons cause degrading of the symmetry of the parent molecules. Introductions of the substituents change their ionization potentials, which can be studied by means of the photoelectron spectroscopy.

In the present letter a photoelectron spectrum of 9-methylanthracene is given in comparison with the spectra of anthracene,[1, 3] and the first few π-bands are assigned with the aid of CNDO and INDO calculations.

The photoelectron spectrum illustrated in Fig. 1 was obtained with a Jasco PE-3 spectrometer. The experimental details were reported in Ref. (5). The target chamber was maintained at 136±1 °C. Commercial 9-methylanthracene was purified by sublimation. The resolution of the spectrum was about 40 meV in the whole region.

Molecular orbitals of anthracene were calculated by use of the geometrical parameters obtained by a X-ray diffraction analysis.[6] For 9-methylanthracene, the C-C bond length between the C^9 and the methyl carbon was assumed 1.51 Å.

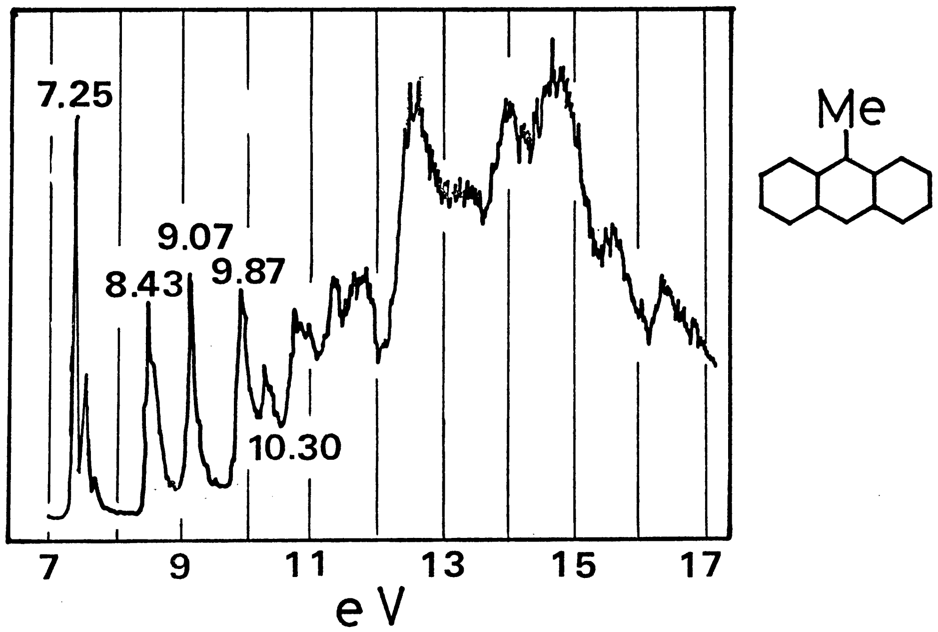

Fig. 1 The photoelectron spectrum of 9-methylanthracene observed at 136±1 °C.

Considering the free rotation of the methyl group around the C^9 - methyl carbon axis,7) the following alternative models were taken into account for the position of the methyl hydrogen atoms: one of the hydrogen atoms is on the anthracene ring plane (position I), or one of the C-H bonds of the methyl group is perpendicular to the ring plane (position II). Since semi-empirical all-electron calculations are known to give too high orbital energies for the σ-levels relative to π-orbital energies (1.5~2.0 eV, according to Refs. (1) and (2)), only the π-orbital energies and ordering were chosen.

The spectrum for anthracene was reported by Boschi, Murrell, and Schmidt1), is shown in Fig. 2. As in the case of anthracene, the first five bands are identified with the π band.1, 3) In correspondence with the vertical ionization potentials for anthracene, 7.47, 8.57, 9.23, 10.26, and 10.4 eV (shoulder of the 10.26 eV peak),1) the first five π bands for 9-methylanthracene observed in the present study are 7.25, 8.43, 9.07, 9.87, and 10.30 eV. Thus introduction of a methyl group into the anthracene ring system results in the splitting of the 10.26 and 10.4 eV bands for anthracene into 9.87 and 10.30 eV. This fact can be understood by the inductive

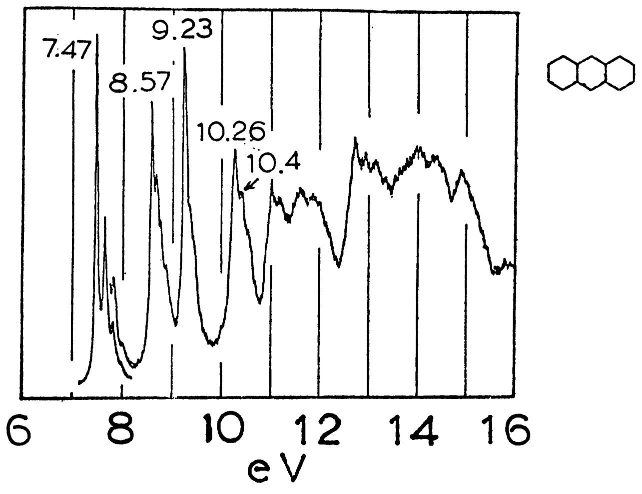

Fig. 2 The photoelectron spectrum of anthracene (Ref. (1)).

effect of the methyl group[8] or by the hyperconjugation[9] of the methyl group with the anthracene ring system.

A conspicuous progression with intervals of 1450 cm^{-1} is observed in the first band. This vibrational structure can be interpreted as a normal mode, in which an alternate stretching of consecutive C-C bonds is mainly involved.[1]

The ionization potentials for anthracene and 9-methylanthracene are listed in Table I, and the results of CNDO and INDO calculations are listed in Table II. Though two different positions of the methyl hydrogen atoms was assumed in the calculations, the point group of 9-methylanthracene was regarded as C_{2v} since only the π bands are

Table I

Ionization potentials of the first five π-bands in eV

anthracene	*	7.47	8.57	9.23	10.26	10.4
	**	7.41	8.55	9.16	10.16***	
9-methylanthracene		7.25	8.43	9.07	9.87	10.30

* Ref. (1)

** Ref. (3)

*** two π-bands

concerned so that it is sufficient to take account of the skeletal carbon atoms alone. In Table II symmetry designations are also given. For the orbital energies of 9-methylanthracene calculated in position I, the MO's coefficients for σ- and π-levels were easily assigned. However, calculations based on position II resulted in some levels where σ- and π-levels were mixed with each other. This mixing occurred only when the MO's coefficient of the methyl carbon had a large value, and the order of the mixing energies was nearly equal to or less than 0.3 eV.

Table II

Calculated orbital energies in eV and symmetry designations of the first several π-bands

anthracene	CNDO	-10.01	-12.55	-14.06	-17.17	-17.60
	INDO	-9.41	-12.01	-13.47	-16.59	-17.02
		$2b_{2g}$	$2b_{3g}$	$1a_u$	$1b_{2g}$	$2b_{1u}$
9-methyl-anthracene in position I	CNDO	-9.72	-12.55	-14.02	-15.89	-17.47
	INDO	-9.17	-12.00	-13.45	-15.42	-16.89
9-methyl-anthracene in position II	CNDO	-9.75	-12.58	-14.04	-15.84 -16.01	-17.49
	INDO	-9.21	-12.04	-13.48	-15.40 -15.60	-16.91
		$4b_1$	$3a_2$	$2a_2$	$3b_1$	$2b_1$

The energy diagrams of photoelectron spectra and the results of MO calculations are illustrated in Fig. 3. Except for the absolute values of the ionization potentials, the MO calculations explain the effects of the methyl group on the photoelectron spectrum of 9-methylanthracene. The ionization potential of the first π band assigned as $4b_1$ ($2b_{2g}$ of anthracene) is decreased by more than 0.2 eV. The second, $3a_2$($2b_{3g}$), third, $2a_2$ ($1a_u$), and fifth, $2b_1$ (b_{2u}) bands are affected slightly. The fourth band, $3b_1$ ($1b_{2g}$) is raised by about 0.4 eV. These experimental

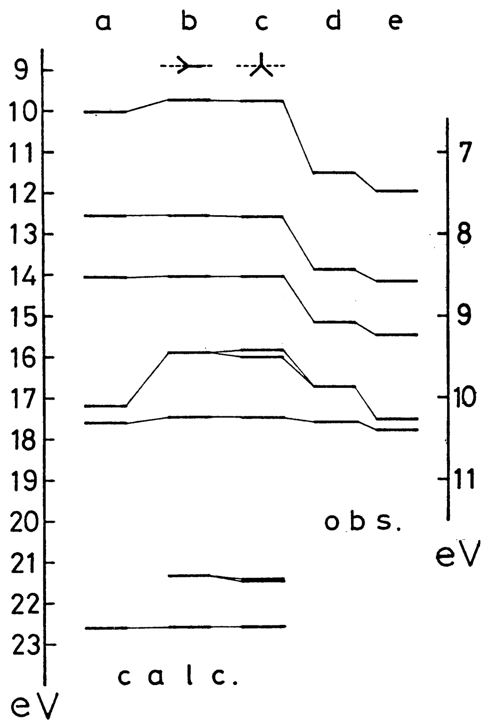

Fig. 3 Energy diagram of anthracene and 9-methylanthracene. a; π orbital energies of anthracene calculated by CNDO, b; π orbital energies of 9-methylanthracene in position I calculated by CNDO, c; π orbital energies of 9-methylanthracene in position II calculated by CNDO, d; observed peak positions for 9-methylanthracene, e; peak positions for anthracene given in Ref. (1)

findings are consistent with the results of the MO calculations listed in Tables I and II.

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