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Ultraviolet Photoelectron Studies of Methyl-Substituted Benz[*a*]anthracenes

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Abstract: Ultraviolet photoelectron spectroscopy has been employed to investigate the electronic structure of 14 methyl-substituted benz[*a*]anthracenes including the carcinogenic 6-methyl, 7-methyl, 8-methyl, 12-methyl, 7,12-dimethyl, and 4,7,12-trimethyl derivatives. The ionization potentials of the six highest occupied π orbitals in all of these molecules have been measured and assigned with the aid of spectroscopically parameterized molecular orbital calculations. For the molecules investigated, trimethyl substitution reduced the first ionization potential of benz[*a*]anthracene more than dimethyl substitution, which in turn caused a larger perturbation than monomethyl substitution. The reduction in ionization potential associated with methyl substitution is sometimes large. For example the vertical ionization potential of 7,12-dimethylbenz[*a*]anthracene is almost 0.4 eV lower than that of benz[*a*]anthracene. However, no simple correlation was found to occur between the ionization potentials of different methyl-substituted benz[*a*]anthracenes and their varying carcinogenic activities. Of the ten monomethyl-substituted benz[*a*]anthracenes studied, it was found that the 7-methyl and 12-methyl derivatives have the lowest ionization potentials. These spectroscopic results correlate well with the description of electron distribution in the highest occupied molecular orbital (π_1) in benz[*a*]anthracene provided by the molecular orbital calculations. According to the calculations the π_1 orbital has highest electron density at the 7- and 12-positions. The spectroscopic results are also consistent with the observation that the trapping of ground-state radical cations of benz[*a*]anthracene by the electron donor, pyridine, occurs most readily at the 7- and at the 12-positions.

Previous studies of polycyclic aromatic hydrocarbons indicate that UV photoelectron spectroscopy can yield very detailed descriptions of valence electronic structure in these molecules. For example, the photoelectron spectrum of benz[*a*]anthracene contains six highly resolved bands arising from the highest occupied π molecular orbitals.[1] In the present investigation, photoelectron measurements have been carried out for a series of methyl-substituted benz[*a*]anthracenes which exhibit widely varying carcinogenic potency. The molecules which have been investigated include benz[*a*]anthracene (I) and 2-methyl- (II), 3-methyl- (III), 4-methyl- (IV), 6-methyl (V), 7-methyl- (VI), 8-methyl- (VII), 9-methyl- (VIII), 10-methyl- (IX), 11 methyl- (X), 12-methyl- (XI), 3,9-dimethyl- (XII), 4,12-dimethyl- (XIII), 7,12-dimethyl- (XIV), and 4,7,12-trimethylbenz[*a*]anthracene (XV).

One goal of the present study has been to examine a theory of hydrocarbon carcinogenesis which stresses the importance of radical cation intermediates. Within the framework of this theory, it has been suggested that the varying carcinogenic activity of methyl-substituted benz[*a*]anthracenes may be related to their ionization potentials.[2,3]

In addition to providing ionization potentials, the present study which involves a large number of methyl-substituted benz[*a*]anthracenes offers the opportunity to spectroscopically probe the π-electron distribution in benz[*a*]anthracene. In earlier studies of heterocyclic aromatic molecules it was found that methyl substitution often gives rise to a photoelectron perturbation pattern which reflects π-electron distributions. For molecules such as uracil[4] and cytosine,[5] the ionization potentials of the two uppermost occupied π orbitals are most destabilized by methyl substitution of those positions where electron density in these orbitals is highest. The present study has focused upon an examination of electron density in the highest occupied π_1 orbital of benz[*a*]anthracene.

This study also points out relationships between photoelectron data and the reaction properties of benz[*a*]anthracene radical cations since photoelectron measurements provide direct information about the energies of radical cation states.

Experimental Section

Photoelectron spectra were measured with a Perkin-Elmer PS 18 photoelectron spectrometer equipped with a heated probe and a HeI lamp. Values of vertical ionization potentials reported here represent the mean of measurements taken from three spectra. The results were reproducible to within ±0.03 eV. Temperatures at which the spectra were measured are given in Table I.

Benz[*a*]anthracene (I) was purchased from the Eastman Kodak Company (Rochester, N.Y.), and 7,12-dimethylbenz[*a*]anthracene (XIV) was purchased from the Sigma Chemical Co. Compounds II, V–VII, X, and XI were provided by Professor Melvin Newman. Compounds III, IV, VIII, IX, XII, XIII, and XV, were prepared by using previously reported methods.[6]

Results and Discussion

In the low-energy region, 7.0–10.5 eV, the spectra of all of the compounds studied except 7-methylbenz[*a*]anthracene (VI) and 11-methylbenz[*a*]anthracene (X) contain six well-resolved bands. This is demonstrated in Figure 1 which shows spectra obtained for benz[*a*]anthracene and 7,12-dimethylbenz[*a*]anthracene. For molecules VI and X, the sixth band is poorly resolved and lies in an energy region where the π and σ manifolds of orbitals overlap. For these two molecules only approximate values of the sixth ionization potential can be obtained.

The first figure shows the photoelectron spectra of benz[*a*]anthracene and 7,12-dimethylbenz[*a*]anthracene (XIV). Each of the spectra exhibits resolved bands arising from the six highest occupied orbitals. In XIV each of these orbitals is destabilized more than 0.2 eV compared to benz[*a*]anthracene. The first ionization potential of 7,12-dimethylbenz[*a*]anthracene is 0.36 eV less than that of benz[*a*]anthracene.

Table I summarizes the photoelectron measurements for all of the molecules studied. The table lists the molecules studied in order of decreasing first ionization potential.

In addition to the photoelectron data obtained here, Table I also lists vertical ionization potentials previously reported[1] for the six highest occupied orbitals of benz[*a*]anthracene. A comparison

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Table I. Vertical Ionization Potentials of Upper Occupied π Orbitals[a-c]

benz[*a*]anthracenes	π_1	π_2	π_3	π_4	π_5	π_6
unsubstituted [114 °C]	7.46 (7.47)	8.07 (8.05)	8.87 (8.86)	9.41 (9.39)	9.96 (9.95)	10.41 (10.41)
6-methyl [103 °C]	7.33	7.93	8.66	9.28	9.87	10.16
8-methyl [112 °C]	7.33	7.98	8.70	9.23	9.79	10.26
9-methyl [115 °C]	7.31	7.93	8.72	9.16	9.81	10.18
2-methyl [100 °C]	7.30	7.93	8.63	9.27	9.78	10.27
4-methyl [120 °C]	7.30	7.87	8.69	9.15	9.78	10.22
10-methyl [110 °C]	7.30	7.96	8.71	9.26	9.77	10.26
11-methyl [100 °C]	7.30	7.94	8.69	9.23	9.71	~10.3
3-methyl [114 °C]	7.29	7.87	8.68	9.17	9.74	10.27
12-methyl [100 °C]	7.27	7.95	8.73	9.21	9.73	10.11
7-methyl [114 °C]	7.24	7.93	8.72	9.26	9.67	~10.3
3,9-dimethyl [125 °C]	7.20	7.79	8.62	9.00	9.66	10.18
4,12-dimethyl [107 °C]	7.18	7.83	8.61	9.03	9.64	9.99
7,12-dimethyl [107 °C]	7.10	7.85	8.62	9.13	9.49	10.01
4,7,12-dimethyl [129 °C]	7.06	7.76	8.53	8.95	9.40	9.89

[a] All energies given in eV. [b] For benz[*a*]anthracene, values in parentheses are those previously reported in ref 1. [c] Temperatures at which spectra were measured are given in square brackets.

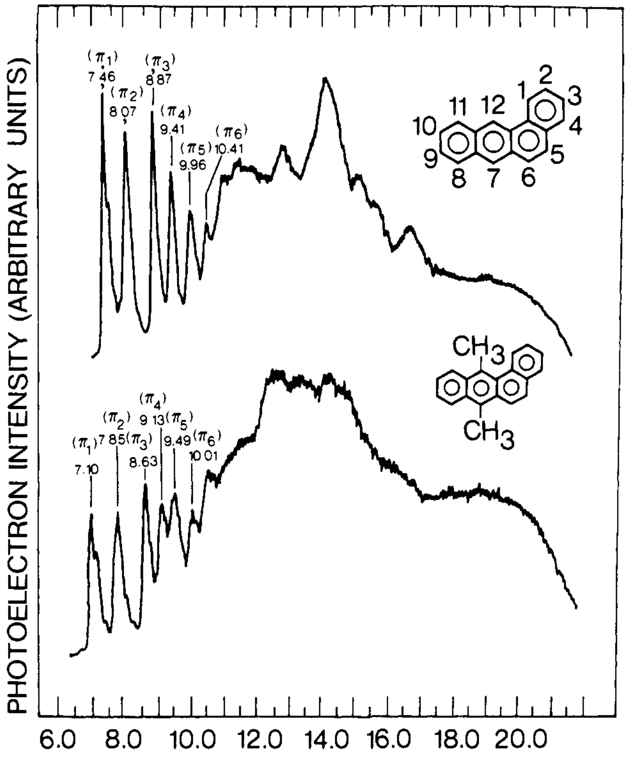

Figure 1. He(I) photoelectron spectra of benz[*a*]anthracene and 7,12-dimethylbenz[*a*]anthracene. Assignments and vertical ionization potentials are given for the six highest occupied orbitals.

of the two sets of data indicates that the agreement is good. In Table I and Figure 1 the assignment of the six lowest energy bands to π orbitals is also consistent with the earlier assignment of the spectrum of benz[*a*]anthracene.[1]

The photoelectron data for molecules I, V, VI, XI, XII, and XV has been compared with ionization potentials obtained from solution studies involving charge-transfer spectroscopy[2] and polarographic measurements.[7] This comparison indicates that while the vertical ionization potentials reported here are 0.1–0.3 eV lower than those obtained in solution, the relative ordering in solution is the same as that in the gas phase.

Because of the electron-donating properties of methyl groups, the results in Table I indicate that the first ionization potentials decrease in the order benz[*a*]anthracene > methylbenz[*a*]anthracenes > dimethylbenz[*a*]anthracenes. Of all the molecules studied, 4,7,12-trimethylbenz[*a*]anthracene has the lowest ionization potential. The results also indicate that methyl substitution at the 7-position or at the 12-position more efficiently reduces the ionization potential of benz[*a*]anthracene than monomethyl substitution at the other positions probed in these studies. However, it is interesting to note that differences between the first ionization potentials of different momomethyl-substituted benz[*a*]anthracenes are not large. The first ionization potentials of all these derivatives fall within a range of less than 2 kcal/mol.

In order to further consider the present spectral assignments, the spectroscopic results have been compared with energy levels predicted by CNDO/S3 molecular orbital calculations.[8] This computational procedure has been parameterized explicitly to fit the spectroscopic data from aromatic hydrocarbons so that the computed molecular orbital eigenvalues correspond directly to the energies required for formation of cation radicals in various electronic states from neutral parent molecules in the ground state.

The geometries of molecules I–XI employed in the calculations were obtained from crystallographic data on benz[*a*]anthracene,[9] which has a planar conformation. Geometries for molecules XI, XIII, and XV, which contain a methyl group in the 12-position, were based on the crystal structures of 7,12-dimethylbenz[*a*]anthracene[10,11] which has a nonplanar structure. In 7,12-dimethylbenz[*a*]anthracene the angular ring is tilted 21.2° out of the plane containing the anthracene ring system. The methyl group at the 12-position is 12.0° out of this plane.[10]

An examination of the computational results indicates that the absolute ionization potentials predicted by CNDO/S3 are ~1 eV too high. However, the energetic spacings of the upper occupied π orbitals which are predicted by CNDO/S3 are similar to those observed experimentally. The CNDO/S3 results indicate that the five lowest energy photoelectron bands all arise from π orbitals. This is in agreement with the earlier assignment of the spectrum of benz[*a*]anthracene.[1]

While the calculations accurately treat the five highest occupied orbitals they predict that for all of the molecules studied the ionization potential of the highest occupied σ bonding orbital is less than that of the sixth highest occupied π orbital (π_6). Furthermore, for all the molecules except the 3,9- and the 4,12-dimethyl derivatives the CNDO/S3 calculations predict that the ionization potential of the second highest occupied σ orbital is also lower than that of the π_6 orbital. This is probably an artifact of the computational method. As noted in an earlier study of aromatic hydrocarbons,[12] the energetic interspacing of the π and σ

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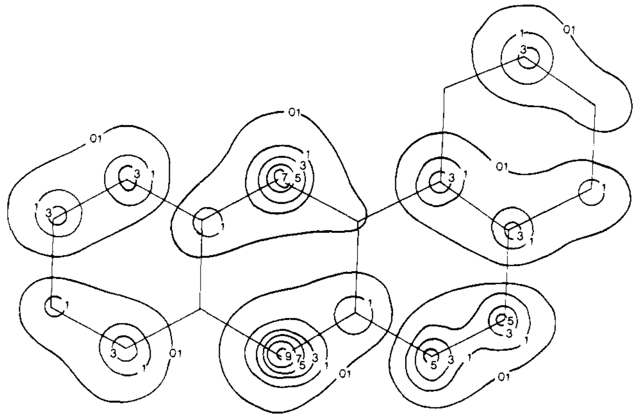

Figure 2. Electron distribution in the highest occupied orbital of benz[*a*]anthracene as predicted by CNDO/S3 calculations. The map shows the electron distribution at 0.25 Å above the plane of the molecule. Values of electron density, denoted on the contours, are normalized to the maximum density in the orbital.

manifolds of orbitals predicted by CNDO/S3 is approximate. Often calculations of this type predict σ orbital binding energies which are too small relative to π orbital binding energies.

In addition to yielding accurate assignments for the five highest occupied orbitals, the orbital perturbation pattern associated with methyl substitution is generally well predicted by the CNDO/S3 calculations. For example, the calculations accurately predict that of the monomethyl-substituted benz[*a*]anthracenes studied, the 7- and 12-methyl derivatives have the lowest ionization potentials.

Insight into the methyl-substitution perturbation pattern of the π_1 orbital in benz[*a*]anthracene is provided by consideration of the electron distribution associated with this orbital. Figure 2 shows an electron density map for the π_1 orbital obtained from CNDO/S3 results on benz[*a*]anthracene. The map was constructed in a manner described previously.[4] As expected from the spectroscopic results, Figure 2 indicates that the highest electron density in the π_1 orbital occurs at the 7- and 12-positions. In benz[*a*]anthracene the highest occupied π orbital is most effectively perturbed by methyl substitution at those positions where the orbital has greatest electron density.

The present spectroscopic results reflect the reaction properties of ground-state radical cations of benz[*a*]anthracene. Studies of product distributions of pyridinum salts formed in reactions of benz[*a*]anthracene radical cations with the electron donor pyridine indicate that pyridine substitution occurs most readily at the 7- and at the 12-positions.[3] The product distribution in such reactions apparently reflects the total charge distribution in the reactant radical cations. The ground-state cation is predicted to have greatest positive charge at the reactive sites.[3,13]

As indicated by Figure 2, the radical cation reaction properties, like the perturbation pattern of the π_1 ionization potential, are related to the high electron density of the π_1 orbital at the 7- and at the 12-positions. For benz[*a*]anthracene, which is nonpolar and highly aromatic, it is reasonable that centers of high positive charge in the radical cation ground state arise from centers of electron deficiency in the highest occupied orbital which is only half-filled.

Much current interest in the chemistry of methyl-substituted benz[*a*]anthracenes arises from the widely varying carcinogenic potency exhibited by these molecules.[14-19] For example, benz[*a*]anthracene and most monomethyl-substituted benz[*a*]anthracenes are at most only marginally carcinogenic. However, monomethyl substitution at the 6-, 7-, 8-, or 12-positions enhances the potency of benz[*a*]anthracene dramatically, and 7,12-dimethylbenz[*a*]anthracene is among the most potent carcinogenic hydrocarbons currently known.

In an attempt to explain these structure–activity relationships and other biochemical observations, a radical cation theory of hydrocarbon carcinogenesis has been considered in several studies.[2,3,19] According to this theory, radical cations are the ultimate carcinogens derived from polycyclic aromatic hydrocarbons. It has been suggested that these radical cations react with critical cellular sites, presumably DNA, leading to the induction of cancer. The formulation of this theory has led to the prediction that for compounds with similar charge distributions, such as the present series of methyl-substituted benz[*a*]anthracenes, carcinogenic potency increases as the hydrocarbon ionization potential decreases.[2]

In agreement with the radical–cation hypothesis, the present results indicate that an effective way of decreasing the ionization potential of benz[*a*]anthracene and enhancing carcinogenic potency is via methyl substitution at the 7- or at the 12-positions. However, a further examination of the data indicates that there are important discrepancies. In apparent contradiction of the theory, the ionization potentials of the 6- and 8-methylbenz[*a*]anthracenes, which both have values of 7.33 eV, are almost identical with the ionization potentials of the noncarcinogenic 9-, 10-, and 11-methylbenz[*a*]anthracenes, which have values of 7.31, 7.30, and 7.30 eV, respectively.

For methyl-substituted benz[*a*]anthracenes the phototelectron data indicate that there is no simple correlation between the π_1 ionization potentials and carcinogenic potency. However, the electronic perturbation of benz[*a*]anthracene due to methyl substitution can be significant. The present results indicate that the π_1 ionization potential of 7,12-dimethylbenz[*a*]anthracene is 0.38 eV lower than that of benz[*a*]anthracene and that the total destabilization of the six highest occupied π orbitals due to dimethyl substitution at the 7- and 12-positions is more than 1.9 eV. Such a perturbation of π orbital structure is certainly large enough to alter reactive and binding properties in a manner which could ultimately influence the biochemical activity of 7,12-dimethylbenz[*a*]anthracene and its metabolites.

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