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ELECTRON SPECTRA OF RADICAL CATIONS OF HETEROANALOGS

OF INDENE

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The electron absorption spectra of the radical cations of indene heteroanalogs were studied by nanosecond laser photoexcitation. The absorption bands in the 450-650 nm region were assigned on the basis of absorption and photoelectron spectroscopy.

By means of nanosecond pulsed photoexcitation we have previously [1] studied the visible portion of the electron absorption spectra of indene (I), indole (II), 1-ethylindole (III), 2-methylindole (IV), 1-methylbenzimidazole (V), 2-ethylindazole (VI), and benzoxazole (VII). These molecules are characterized by absorption in the 450-650 nm region. From general considerations it follows that in this spectral range the radical cations of benzoxazole, indazole (VIII), benzimidazole (IX), and their derivatives (i.e., heterocyclic systems containing a pyridine nitrogen) can show two types of electron transitions, viz., the $\pi \to \pi^*$ and $n \to \pi^*$ types. According to the data of [1] the absorption bands in the 450-650 nm region correspond only to $\pi \to \pi^*$ transitions. This assignment is based on their quite high intensity at the absorption maximum ($\log \epsilon > 3$) and the bathochromic shift of these bands when the dimensions of the π-system are increased. More detailed information about the nature and location of the long-wave transitions can be obtained from the concurrent application of electron spectroscopy of the radical cations and the photoelectric spectroscopy (PES) of the parent molecules.

The possible use of PES in this connection has been demonstrated in a number of studies, which have been discussed in part in [2]. The basis for comparing these spectral methods is the fact that the difference between the first and subsequent ionization potentials of a neutral molecule enables us to predict the energy ($h\nu_{cr}$) of the electron excitation of a particular doublet state of a radical cation ($\tilde{X}-\tilde{A}$ etc. [3]) (Fig. 1). Naturally it is difficult to expect a more precise correspondence, first of all because of the difference in ground-state equilibrium configurations of the radical cation and parent molecule, and also the difference in the phase states in which the respective experiments are most usually carried out [2]. Nevertheless it will be shown below that with indene and its heteroanalogs (planar heteroaromatic systems), PES enables us to determine both the energy and the type of radical-cation absorption bands that are located in the visible region.

Because information is lacking for compounds III, V, and VI concerning the energy gaps between the occupied molecular orbitals (MO), the photoelectron spectra of these molecules were studied. Assignment of transitions in the PES of these compounds was based on the linear correlation with the respective energies in the PES of the unsubstituted compounds II, VIII, and IX [4, 5], and with the electron transition energies ($h\nu_{et}$) in the spectra of donor-acceptor complexes (Table 1). It is noteworthy that the donor-acceptor complexes of II-V with strong electron acceptors show two charge-transfer bands (CTB), the energies of
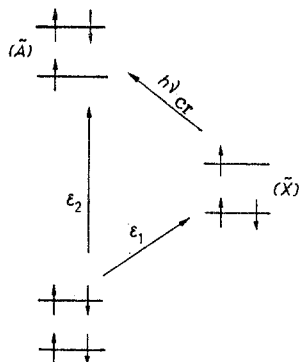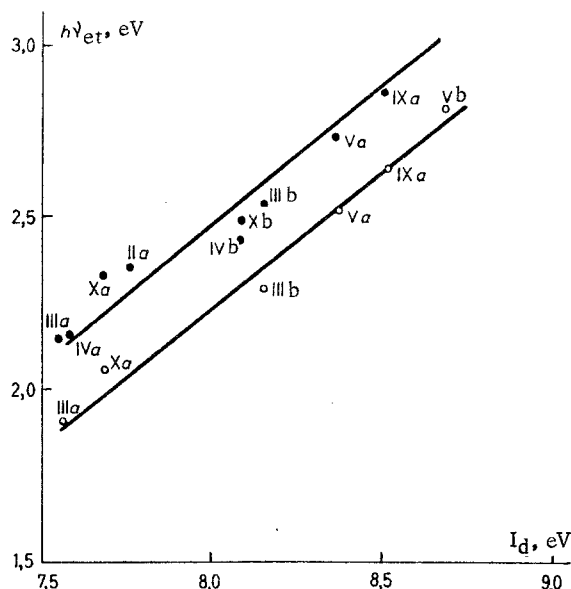
Fig. 1   Fig. 2

Fig. 1. Energies corresponding to the photoelectron spectrum of a molecule (ε_1, ε_2) and the long-wave transition (hv_{cr}) in the spectrum of its radical cation.

Fig. 2. Transition energy function with charge shift for the donor—acceptor complexes of chloranyl ( ) and 7,7,8,8—tetracyano-quinodimethane ( ) on the first (a) and second (b) ionization potentials of idene heteroanalogs (X — carbazole [6]).

TABLE 1. Conventional Assignment and Ionization Potentials of Compounds III, V, and VI

Com-pound	Conventional assignment	Ionization potential, eV	Com-pound	Conventional assignment	Ionization potential, eV	Com-pound	Conventional assignment	Ionization potential, eV
III	π_5*	7,55	V	π_5	8,36	VI	π_5	7,85
	π_4	8,15		π_4	8,62		π_4	8,75
	π_3	9,57		π_3	10,44 (9,93)†		π_3	9,99 (9,99)†

*Numeration from first occupied MO (π_5).
†Ionization potential of unshared electron pair of nitrogen.

which correlate with the first two ionization potentials (Fig. 2)*. In the case of weaker electron donors (e.g., IX) and/or weak π-acids the short wave CTB strongly overlaps the spectrum of the electron acceptor used, and its energy cannot be reliably determined.

Table 2 shows the values of the energy gap between the first (π_5) and third (π_3) occupied π-type MO ($\Delta\varepsilon_{\pi_5\pi_3}$) of the test compounds and the energy of the long-wave maximum in the radical cation spectrum. Comparison of the results shows that within the limits of experimental error hv_{cr} coincides with $\Delta\varepsilon_{\pi_5\pi_3}$. Thus in the 450-650 nm range the radical cation absorption spectrum of indene and its heteroanalogs is due to excitation of an electron from an inner filled π_3-MO to a partially occupied π_5-MO. The transitions produced by the excitation of π_4-MO electrons and the n → π^* transitions in the radical cation spectra of V and VII are probably located in the IR region of the spectrum. Possibly in the case of the indazoles the absorption band due to a n → π^* transition overlaps the more intense π → π^* band that is located in the same region of the spectrum.

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*The location of the CTB maxima was determined by analyzing the shape of the band, analogously to [6].

TABLE 2. Energy Gaps between Occupied MO of a Neutral Molecule and the Energy of Long-Wave Transitions in the Spectrum of Its Radical-Cation (acetonitrile)

Compound	$\Delta\varepsilon_{\pi_5-\pi_3} \pm 0.05^* $ eV	$h\nu_{cr} \pm 0.03$ eV
I	2,15 † [4]	2,18
II	2,09 [4]	2,11
III	2,02	2,09
IV	2,14 † [7]	2,31
V	2,08 (1,57)	2,09
VI	2,14 (2,14)	2,09
VII	2,42 † [4] (1,72)	2,45
VIII	2,09 † [4] (2,09)	2,10
1-Methylindole	2,10 † [7]	2,05 [8]
Benzothiophene	1,89 † [7]	1,94 ‡

*In parentheses, the difference in ionization potential of π_5-MO and the unshared electron pair of the nitrogen atom.
†For I, II, VII, VIII, and benzothiophene, the difference in the vertical ionization potentials; for IV and 1-methyl-indole, the difference in adiabatic ionization potentials.
‡Broad band, spread over the $\lambda > 650$ nm region. Data at observed maximum.

EXPERIMENTAL

Radical cation spectra of indazole and benzothiophene in the visible region were obtained by laser photolysis during the reaction of photoexcited quinones with these compounds in acetonitrile. The charge transfer bands of the complexes of the test compounds with p-chloranil and 7,7,8,8-tetracyanoquinodimethane in dioxane were recorded on a Specord M-40. Photoelectron spectra were obtained on a ÉS-3201 electron spectrometer. The He(I) resonance band (21.21 eV) was used for excitation. Measurements were carried out in the 60–120°C range. The energy scale was calibrated from the first ionization potentials of Ar (15.76 eV) and chlorobenzene (9.06 eV). The error in the determination of the ionization potentials for the first four photoelectron bands was 0.05 eV.

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