ELECTRONIC ABSORPTION SPECTRA OF CATION RADICALS AS A SOURCE OF INFORMATION REGARDING THEIR CONFORMATIONS

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On the basis of differences in the energy gaps between the molecular orbitals of the π type of biphenyl, 2,2'-dithienyl, 2-phenyl(thienyl)pyrrole, 2-phenylselenophene (photoelectronic spectroscopy), and their cation radicals (nanosecond laser spectroscopy) it was shown that ionization causes transition to a more planar molecular conformation.

Satisfactory coincidence of the energy gaps (Δ) between the π orbitals (π MO) of the neutral molecule and its cation radical has been established for planar aromatic and heteroaromatic systems [1, 2]. In the case of cation radicals of compounds that have a nonplanar orientation of the fragments in the neutral state the difference in the energies of the partially occupied and doubly occupied π MO may differ substantially from the corresponding Δ value of the neutral molecule [3].

In the present research we investigated the electronic absorption spectra of the cation radicals of 2-phenyl(thienyl)pyrrole, 2-phenylselenophene, 2,2'dithienyl, and some biphenyl derivatives. The energy gaps between the π MO of the cation radicals found from these spectra were compared with the Δ values of the neutral molecules calculated from data obtained from photoelectronic spectroscopy (PES), and the problem of the change in the conformation of the molecules upon ionization was examined. The ionization potentials (I) of the neutral compounds and the energies of the electron transitions (ΔE) in the visible region of the spectrum of their cation radicals are presented in Table 1. For these relatively simple molecules the orbital structure and its relationship to the three-dimensional structure and the positioning of the long-wave electron transitions in the UV spectra of the cation radicals can be readily understood within the framework of the concepts regarding fragment π MO. It follows from the orbital correlation diagram that interaction of the fragment π MO leads to the development of two types of molecular orbitals (Fig. 1). These are the π_4 and π_5 MO, which have a node at the bonding atom, and the π_3 and π_6 MO, the energies of which are determined by the degree of overlapping of the fragment orbitals, i.e., the angle of rotation of the aryl (hetaryl) fragments. The transitions between the singly occupied π_6 MO and the deep-lying doubly occupied π_3 MO are also responsible for the development of an absorption band in the visible region of the spectrum of the cation radical ($\Delta E_{3,6}$; Fig. 1, Table 1). The transitions from the high-lying π_4 and π_5 MO to the partially occupied level of the cation radical are located in the IR region of its spectrum.

It is known that in the gas phase the biphenyl (I) molecule has a nonplanar orientation of the fragments with a dihedral angle beteen them of $\varphi = 42°$ [6]. The energy gap $\Delta_{3,6}$ found for this phase state by photoelectronic spectroscopy as the difference between ionization potentials I_4 and I_1 is equal to 1.48 eV for this compound (Table 1). In the crystal the conformation of the I molecule becomes planar [7]. An investigation of the biphenyl cation radicals in the solid phase was made by pulse radiolysis [8]. Under these conditions (77°K, CCl_4) the difference between the partially occupied π_6 MO and the completely occupied π_3 MO of the cation radical of I (~1.8 eV [8]) substantially exceeds the $\Delta_{3,6}$ value found for the I molecule in the gas phase. In the liquid (295°K, CH_3CN) $\Delta E_{3,6}$ increases even more (1.87 eV) and approaches the $\Delta_{3,6}$ value of fluorene II – an analog of biphenyl that is known to be planar. The energy of the electron transition under discussion in the UV spectrum of the cation radical of II, on the other hand, virtually coincides with the $\Delta_{3,6}$ value of the neutral form (Table 1). These data constitute evidence

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TABLE 1. Energy Characteristics of the Neutral Molecules and Their Cation Radicals

Compound	Ionization potentials, eV				$\Delta_{3,6}$, eV	$\Delta E_{3,6}$, eV	δ, eV
	I_1	I_2	I_3	I_4			
I*	8,34	9,04	9,20	9,82	1,48	1,87	0,39
II*	7,91	8,77	9,09	9,84	1,93	1,94	0,01
III	8,28	9,49	9,49	9,71	1,43	1,84	0,41
IV	7,94	9,11	9,22	9,82	1,88	2,11	0,23
V	7,61	8,89	9,19	9,69	2,08	2,34	0,26
VI †	7,41	9,00	9,18	9,45	2,04	2,32	0,28
VII	8,08	8,81	9,25	9,88	1,80	2,03	0,23
VIII	7,70	9,18	9,55	9,55	1,85	2,17	0,32

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*Photoelectronic spectrum from [4].

†From [5]. According to the assignment made in this study, δ(VI) = 0.55 eV.

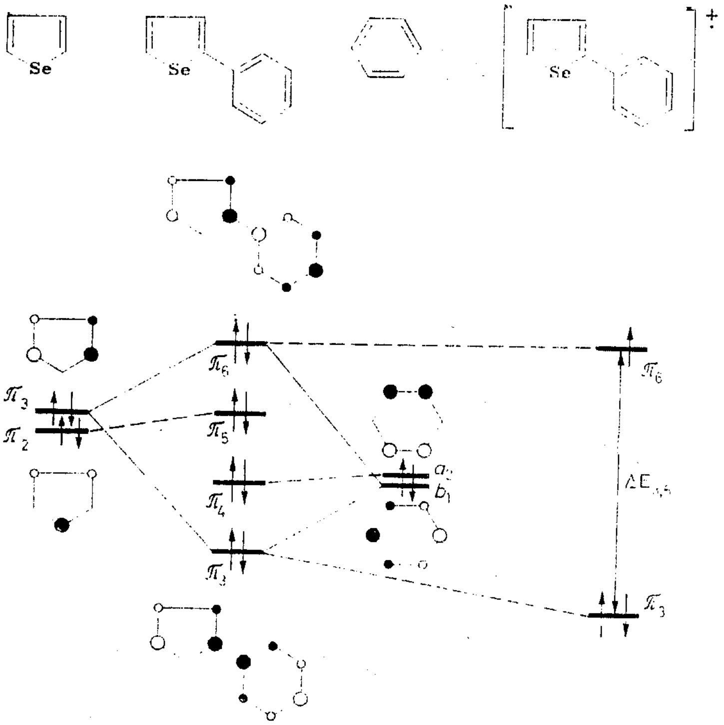

Fig. 1. Orbital correlation diagram of selenophene, benzene, and 2-phenylselenophene and its cation radical (overlapping is disregarded). The energy spacing of the molecular and fragment orbitals is in accordance with the results of photoelectronic spectroscopy. The position of the partially occupied level of the cation radical is shown arbitrarily.

that the change in $\Delta_{3,6}$ upon ionization is associated with conformational restructurings of the molecule of I and that I exists in a conformation that is close to planar in the ionized state.

On the basis of data on molecules that contain two fragments of the same type [9] for situations in which the change in the $\Delta\varphi$ value is comparable to the absolute value of angle φ, it is easy to show that the difference $\delta = \Delta E_{3,6} - \Delta_{3,6}$ is approximated by the equation

$$\delta\ (\mathrm{eV}) \approx 3.3 \sin^2 \Delta\varphi/2. \tag{1}$$

According to Eq. (1), in the ionization of biphenyl $\Delta\varphi = 40 \pm 10°$. A close result (41 ± 10°) was obtained for 4,4'-dichlorobiphenyl (III) (Table 1).

A difference in the three-dimensional structures in the gaseous, liquid, and crystalline states is observed for other similar biphenyl compounds. Thus 3,3'- and 2,2'-dithienyls in the solid phase are also planar [10]. In the gaseous phase the φ angles of the indicated dithienyls are 30° and ~34°, respectively [6, 11]. In the liquid the rotation of the fragments is evidently somewhat smaller. For example, according to data on the Kerr molar constants 2,2'-dithienyl (IV) has $\varphi = 23 \pm 10°$ [12]. Special note is made of the fact that the results of electron diffraction experiments are not in agreement with a "rigid" conformation of IV, and almost free motion of the fragments (twisting vibrations of considerable amplitude) is suggested [10]. According to the estimates of Bucci and coworkers [13], the barrier to internal rotation for dithienyl IV is ~5 kcal/mole. In its ionic forms IV is evidently completely planar. Thus a planar or close-to-planar conformation for 2,2'-dithienyl cations on the basis of NMR data [14]. Thus in the ionization of IV one should have expected the same changes in the energy characteristics as for biphenyl. This is actually observed experimentally (Table 1). Calculation from Eq. (1) leads to $\Delta\varphi = 31 \pm 10°$ for dithienyl IV.

The situation with 1(2)-aryl(hetaryl)-substituted unsaturated five-membered heterocycles is less unambiguous. The results of photoelectronic spectroscopy [15] and data on the dipole moments and from the electronic absorption and NMR spectra [16] constitute indirect evidence for the nonplanar structure of some of them. Nevertheless, a number of experimentally determined values, particularly the dipole moments of 2-hetarylpyrroles, can be explained by the existence of an equilibrium mixture of two planar conformers with syn and anti orientations of the heteroatoms [5]. Nonplanar structures of phenylpyrroles (thiophenes) and 2(3)-(3-hetaryl)selenophenes are predicted by calculations by the extended Hückel method (EHM) [17, 18]. This method simultaneously provides evidence for the planarity of the 2,2' dimers of five-membered heterocycles, which is only in partial agreement with the experimental results [11, 12, 19]. Recent quantum-chemical investigations (INDO, ab initio [5, 20]) have shown that the 2-(2-furyl)- and 2-(2-thienyl)pyrrole molecules have planar three-dimensional structures. At the same time, for example, the photoelectronic spectra of the thiophene analogs of the latter can be explained successfully by a nonplanar model [21]. The changes in the $\Delta_{3,6}$ energy gap that occur in the ionization of 2-phenyl- and 2-(2-thienyl)pyrroles (V and VI) are in agreement only with nonplanar structures of these heterocycles (Table 1). From the results of quantum-chemical calculation (MINDO/3) of 1-substituted 2-phenylpyrroles the energy gap $\Delta_{3,6}$ of pyrrole V is described by the calibration function

$$\Delta_{3,6} = \Delta_0 + 1.03 \cos^2 \varphi.$$

From which, for large changes in the dihedral angle, we obtain

$$\delta \approx 1.03 \sin^2 \Delta\varphi. \tag{2}$$

The difference $\Delta\varphi$ between the neutral molecule and the cation radical of V obtained from the experimental $\Delta_{3,6}$ and $\Delta E_{3,6}$ values (Table 1) by means of Eq. (2) is 30 ± 10°. Since a change in $\Delta_{3,6}$ ($\delta \neq 0$) is observed on passing from the neutral state to the ion-radical state of 2-(2-thienyl)pyrrole (VI), 2-phenyl selenophene (VII), and 2-(4-chlorophenyl)pyrrole (VIII), these compounds also undergo geometrical restructurings.

Thus the data obtained make it possible to conclude that the ionization of nonplanar, unsaturated, molecular systems such as biphenyl is accompanied by significant changes in the conformation.

EXPERIMENTAL

The photoelectronic spectra of III-V, VII, and VIII were obtained with an ES3201 electronic spectrometer at 30-100°C. The energy scale was calibrated with respect to the first ionization potentials of Ar (15.76 eV) and chlorobenzene (9.06 eV). The resonance of the He(1) band (21.21 eV) was used for excitation. The error in the determination of the ionization potentials was ±0.05 eV.

The electronic absorption spectra of the cation radicals were recorded with a laser photolysis apparatus [22]. The cation radicals were obtained by means of reaction of the neutral compounds with electronically excited tetrachloro-1,4-benzoquinone (an electron acceptor) in acetonitrile at 18-22°C.

The calculations by the MINDO/3 method were made by means of the program in [23]. The range of change in φ was 0-90° with an interval of 15°. Optimization of the bond angles of the five-membered heteroring and the lengths of the $C_{(2)}$—$C'_{(1)}$ interfragment bonds was accomplished for each φ value.

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BENZOID-QUINOID TAUTOMERISM IN AZOMETHINES AND THEIR STRUCTURAL ANALOGS.

46.* SYNTHESIS AND REACTIONS OF 2-(N-ISATINOMETHYLENE)-3(2H)-BENZO[b]THIOPHENONE

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Electronic, IR and UV spectroscopy has shown that 2-(N-isatinomethylene)-3(2H)-benzo[b]thiophenone in solution displays photo- and solvatochromism as a result of reversible E → Z isomerization, and it readily undergoes alcoholysis of the lactam bond. The resulting aminovinyl ketones exist as mixtures of the thermodynamically stable E- and Z-isomers.

We have previously shown that N-acylated 2-(N-arylaminomethylene)-3(2AH)-benzo[b]thiophenenones on irradiation with light undergo N → O acyl rearrangement as a result of photochemical Z → E isomerization [2].

The purpose of the present investigation was to synthesize an aminovinyl ketone with an N-acyl group, fixed by an additional bond in the o-position of the N-aryl ring, and to examine its structure, solvato- and photochromism, and in particular the possibility of occurrence of the above-mentioned reaction [2].

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*For Communication 45, see [1].

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