ELECTRONIC ABSORPTION SPECTRA OF PSEUDOAZULENES — BENZO[b]CYCLOPENTA[e]PYRAN DERIVATIVES

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Benzo[b]cyclopenta[e]pyran derivatives were synthesized, and their electronic absorption spectra were recorded. The absorption spectra were calculated by the Pariser—Parr—Pople method. The absorption bands in the spectra of the synthesized compounds were assinged on the basis of an anlysis of the experimental and calculated values obtained in the study. It is shown that the long-wave transition in the spectra of benzo[b]cyclopenta[e]pyrans is realized through charge transfer from the five-membered ring to the six-membered heteroring and is determined to a great degree by the pronounced delocalization of the C—C bonds in the fulvene fragment on passing to the first excited state. The bathochromic shift of the long-wave band when phenyl and styryl substituents are introduced is due to the increase in the energy of the upper occupied molecular orbital as compared with the virtual invariability of the level of the lower vacant molecular orbital.

The data on the electron distribution, reactivities, and electronic absorption spectra obtained for benzo[b]cyclopenta[e]pyran by the MO LCAO method within the Hückel approximation [1, 2] and by the Pariser—Parr—Pople (PPP) method [3] provide evidence for the azulene-like behavior of this class of compounds. The changes in the spectra of azulene and pseudoazulenes that are observed when substituents are introduced depend not only on their number and character but also on their position in the molecules. Experimental data on the effect of only phenyl substituents on the spectra of benzocyclopentapyran have been discussed [4-8], and it has been concluded that the direction and magnitude of the shifts of the absorption maxima approximately coincide with the direction and magnitude for azulenes.

The present research was devoted to an experimental and theoretical study of the absorption spectra of a number of 2-phenylbenzo[b]cyclopenta[e]pyran (2-Ph-BCPP) derivatives (Table 1): the effect of both acceptor and some donor substituents in the 1 and 3 positions on the spectra and the assignment of the absorption bands in them were studied. The absorption spectra were calculated by the PPP method with allowance for 25 singly-excited configurations with a modified program, the algorithm of which is described in [9]. The noncoplanarity of the phenyl groups was taken into account in the calculation by variation of the parameters until they agreed with the experimental values for the C—C bond lengths.

1. Assignment of the Bands in the Absorption Spectra

The long-wave band in the spectrum of I is 96% due to a one-electron transition from the upper occupied molecular orbital (UOMO) to the lower vacant molecular orbital (LVMO) (Table 2). According to an analysis of the distribution of the π charges on the atoms of the molecules in the ground and first excited states (Fig. 1) and the atomic coefficients of the UOMO (ψ_m) and the LVMO (ψ_{m+1}), the transition is accompanied by charge transfer primarily from the five-membered ring to the six-membered heteroring:

$$\begin{aligned}\psi_m(\text{UOMO}) = {} & -0.574\varphi_1 - 0.208\varphi_2 + 0.449\varphi_3 - 0.299\varphi_4; \\ & +0.181\varphi_5 - 0.171\varphi_7 - 0.107\varphi_8 + 0.165\varphi_9; \\ & -0.105\varphi_{10} + 0.391\varphi_{11} + 0.158\varphi_{3'} + 0.102\varphi_{2'}; \\ & -0.117\varphi_{4'} + 0.109\varphi_{6'}; \\ \psi_{m+1}(\text{LVMO}) = {} & +0.209\varphi_1 - 0.291\varphi_2 + 0.092\varphi_3 - 0.263\varphi_4 + 0.237\varphi_5; \\ & -0.301\varphi_6 + 0.330\varphi_8 - 0.512\varphi_9 + 0.302\varphi_{10}; \\ & +0.281\varphi_{11} + 0.189\varphi_{12} + 0.126\varphi_{2'} - 0.132\varphi_{4'}; \\ & +0.128\varphi_{6'} \ (m = 10).\end{aligned}$$

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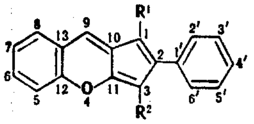
TABLE 1. Electronic Absorption Spectra of 2-Phenyl-BCPP Derivatives



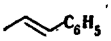
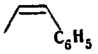
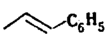
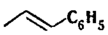
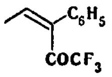
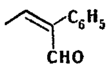
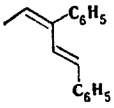
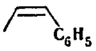
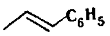
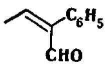
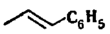
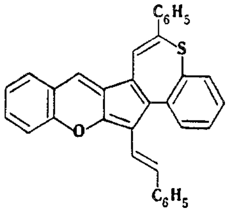
Compound	R¹	R²	λ_{max}, nm (log ε) in tetrahydrofuran	Oscillator force of the long-wave transition (f)
1	2	3	4	5
I	H	H	260 (4,39); 365 (4,44); 470 (2,67)	0,023
II	C_6H_5	H	270 (4,39); 365 (4,37); 512 (2,91)	0,029
III	H	C_6H_5	256 (4,59); 362 (4,43); 510 (2,89)*	—
IV	C_6H_5	C_6H_5	285 (4,64); 365 (4,38); 530 (3,19)	0,054
V	CHO	H	255 (4,22); 300 (4,18); 360 (4,47); 480 (3,39)	0,070
VI	CHO	CHO	286 (4,55); 360 (4,42); 460 (3,40)	0,053
VII	C_6H_5	CHO	260 (4,46); 305 (4,72); 370 (4,38); 490 (3,10)	0,051
VIII	NO_2	H	246 (4,28); 380 (4,49); 500 (3,68)	0,112
IX	C_6H_5	NO_2	265 (4,79); 345 (4,59); 460 (2,84)	0,030
X	$SO_2C_6H_5$	H	250 (4,21); 480 (4,21); 360 (4,46); 470 (3,37)	0,060
XI	C_6H_5	$SO_2C_6H_5$	250; 280 (4,59); 360 (4,44); 470 (3,18)	0,058
XII	$COCH_3$	H	254 (4,16); 290 (4,16); 355 (4,38); 486 (3,59)	0,095
XIII	C_6H_5	$COCH_3$	287 (4,55); 370 (4,25); 480 (3,05)	0,057
XIV	Br	Br	233; 355 (4,46); 496 (2,96)	0,350
XV	C_6H_5	SCN	277 (4,53); 360 (4,38); 486 (3,30)	0,071
XVI	C_6H_5		305 (4,59); 330 (4,58); 570 (3,06)	0,035
XVII	C_6H_5		267 (4,57); 300 (4,48); 541 (2,85)	0,020
XVIII	C_6H_5		270 (4,55); 340 (4,77); 580 (2,65)	0,054
XIX			264 (4,31); 335 (4,78); 610 (2,87)	0,024
XX	C_6H_5		240 (4,48); 275 (4,55); 370 (4,57); 540 (2,97)	0,028
XXI	C_6H_5		255 (4,32); 285 (4,34); 393 (4,45); 530 (3,08)	0,032
XXII	C_6H_5		235 (4,41); 275 (4,42); 350 (4,35); 550 (2,84)	0,012
XXIII	CHO		237 (4,56); 325 (4,61); 375 (4,21); 536 (3,44)	0,062
XXIV	CHO		240 (4,41); 325 (4,69); 375 i (4,20); 570 (3,43)	0,058
XXV		H	235 (4,10); 330 (4,40); 375 (4,52); 550 (2,92)	0,024
XXVI		H	560†	—

Table 1 (Continued)

XXVII		285 (4,40); 378 (4,57); 385 (4,59); 434 (4,11); 565 (2,79)	0,021

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*According to the data in [6] (the solvent was ethanol).
†The compound is unstable (the spectrum of a benzene solution was recorded).

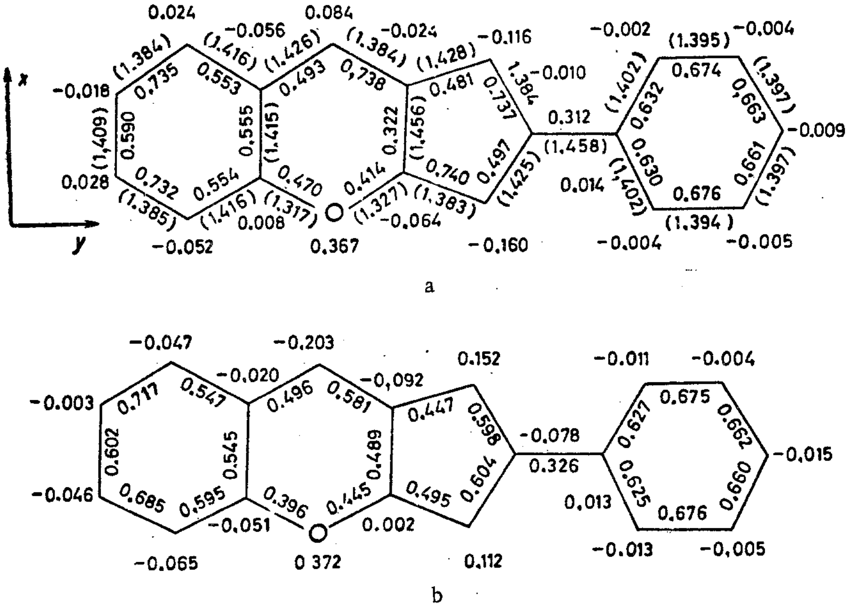
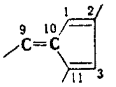


Fig. 1. Molecular diagrams of 2-phenylbenzo[b]cyclopenta[e]-pyran: a) ground state; b) first excited state.

Thus, whereas the overall negative charge on the atoms of the five-membered ring is −0.374 and the overall positive charge in the six-membered heteroring is +0.315 in the ground state, in the first excited state the charge in the five-membered ring changes sign and becomes +0.096 and the charge in the heteroring decreases considerably (to +0.008). In addition, the ring bonds to a certain extent are equalized (Fig. 1). The long-wave transition is polarized at an angle of 66° relative to the x axis of the molecule (Table 2 and Fig. 1); the condensed and attached benzene rings participate weakly in the long-wave transition. In particular, the relatively low intensity of the band is explained by the small change in the dipole moment of the transition ($\Delta\mu$ = 0.400 D). According to the calculations, the long-wave transition is shifted to the red region as compared with the observed maximum of the absorption band. This is explained by the fact that the broad band consists of a number of unresolved vibrational components, of which the electron-vibrational component assigned to the transition between the zero vibrational levels in the ground and excited states is the longest-wave component and corresponds to the calculated transition (Fig. 2). The theoretical analysis of the long-wave electron transition consequently shows that it is determined primarily by the fulvene grouping incorporated as a fragment in the benzooxalene molecule:



The low value of the LVMO energy is due to pronounced delocalization of the bonds in the fulvene fragment.

The second transition at 360 nm is also a one-electron transition and is polarized along the y axis of the molecule. The calculated oscillator force of this transition is

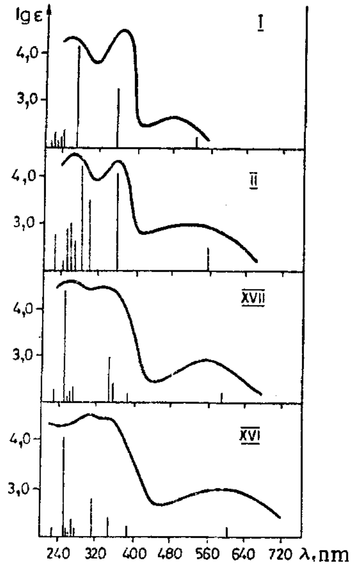


Fig. 2

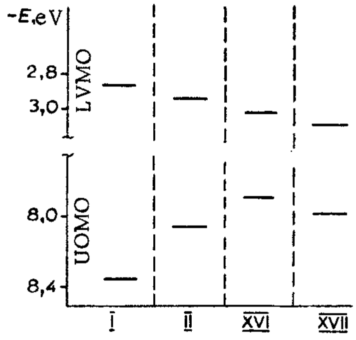


Fig. 3

Fig. 2. Experimental and calculated absorption spectra of I, II, XVI, and XVII according to Table 1.

Fig. 3. Diagram of the energy levels of the UOMO (E_m) and LVMO (E_{m+1}) of I, II, XVI, and XVII according to Table 1.

TABLE 2. Calculation of the Electronic Absorption Spectra of Some Benzo[b]cyclopenta[e]pyran Derivatives

Compound	λ_{max}, nm	F, oscillator force	Polarization relative to the y axis, deg	Compound	λ_{max}, nm	F, oscillator force	Polarization relative to the y axis, deg
I*	530,4	0,069	66,02	XVI	603,1	0,120	63,66
	360,4	0,870	−5,77		388,4	0,113	−46,90
	272,2	1,459	−4,38		348,6	0,211	41,87
	236,2	0,287	−19,06		312,6	0,443	29,60
	234,4	0,080	−60,31		273,9	0,081	−39,04
	230,3	0,052	45,22		270,9	0,182	−1,64
	226,2	0,239	81,26		265,8	0,061	−5,35
					257,9	0,060	−5,69
					256,6	0,062	−53,30
					252,8	1,100	24,29
					229,0	0,082	−31,59
II	558,6	0,152	74,04	XVII	591,3	0,112	65,14
	361,6	0,635	−13,95		384,6	0,115	263,19
	304,4	0,481	38,08		355,5	0,245	31,58
	282,4	0,688	−2,19		309,1	0,491	29,91
	273,9	0,165	−11,26		286,0	0,041	−28,68
	265,6	0,306	−22,75		269,9	0,206	−15,82
	253,4	0,287	−17,42		264,7	0,073	−9,01
	245,3	0,057	70,96		254,6	0,055	−52,20
	241,2	0,092	−66,47		251,8	1,207	22,35
	227,7	0,240	−82,72		228,1	0,091	−31,99

*The numbering of the compounds corresponds to the numbering in Table 1.

an order of magnitude higher than the value for the long-wave transition; this is in qualitative agreement with the experimental data. The calculated λ_{max} value of the transition is in agreement with the observed value. The transition is accomplished between the ψ_{m-1} and ψ_{m+1} orbitals ($\psi_{m-1} \rightarrow \psi_{m+1}$). The remaining bands in the spectrum are due to complex transitions (Table 2).

According to the calculations, the introduction of a phenyl group in the 1 position of I leads to a red shift of the long-wave transition of the spectrum. The red shift is due to drawing together of the UOMO and LVMO energies; the UOMO energy is higher by a factor of approximately five than the relative position of the LVMO energy (Fig. 3). The calculated red shift ($\Delta\lambda$) when a phenyl substituent is introduced is 28.2 nm, as compared with the experimental value of ∼42 nm; the calculated ratio of the oscillator forces of I and II is $f_1/f_2 = 0.45$, as compared with the observed value of 0.5 (Table 1). According to an analysis of the participation of the atomic orbitals (AO) in the formation of molecular orbitals (MO), the marked increase in the UOMO energy is due to the fact that the contribution of the atoms of the phenyl substituent is realized primarily in the UOMO and slightly in the LVMO (Fig. 3). The transition is polarized along the x axis of the molecule. The characteristics (λ_{max}, f, and the polarization) of the second transition remain virtually constant, according to the calculations and the experimental data (Fig. 2). The assignment of the remaining bands is given in Table 2. The nature of the long-wave transition in the spectra of XVI and XVII is similar to the nature of the transitions in the spectra of I and II (Table 2). The strong red shift of this transition is due to further drawing together of the UOMO and LVMO (Fig. 3). The calculations show that the λ_{max} value of the long-wave transition in the spectra of XVI and XVII depends on the cis or trans orientation of the phenyl group: the calculated $\lambda_{max}(trans) - \lambda_{max}(cis)$ difference is 12 nm, as compared with the experimental value of 29 nm. The assignment of the remaining transitions is presented in Table 2.

2. Experimental Absorption Spectra

Since the effect of substituents on the long-wave absorption region is most characteristic for azulene-like systems, we will examine only this portion of the spectrum. It follows from an examination of the absorption spectra (Table 1) that the successive introduction of phenyl substituents in the five-membered ring of I leads to a bathochromic shift of the long-wave band; this shift amounts to 40 nm for one phenyl group and 60 nm for two phenyl groups. The reason for the shift is discussed above. The introduction of electron-acceptor substituents in the 1 position of I leads to a small bathochromic shift of the long-wave band and an approximately fourfold to fivefold increase in its oscillator force, in contrast to azulene, in the spectrum of which one observes a hypsochromic shift when the same substituents are introduced in the 1 or 3 position. However, the introduction of an electron-acceptor substituent in the 3 position of II leads to a 20-40 nm hypsochromic shift of the long-wave band with a 1.5-fold increase in the oscillator force. A trans-styryl group in the 1 position (XVI) gives rise to a 90 nm bathochromic shift, whereas in the 3 position it causes a 60 nm bathochromic shift. Two trans-styryl groups in the 1 and 3 positions (XIX) give rise to a 140 nm bathochromic shift without an appreciable change in the oscillator force. The introduction of electron-acceptor substituents in the α position of the styryl group (XX and XXI) causes a 30-40 nm hypsochromic shift in λ_{max} without affecting the oscillator force. The simultaneous presence of formyl and styryl groups in the 1 and 3 positions, respectively, leads to a 40 nm bathochromic shift and a 3.5-fold increase in the oscillator force.

Thus an analysis of the calculated and experimental values makes it possible to conclude that the long-wave transition in benzoxalene is determined to a great degree by pronounced delocalization of the C—C bonds in the fulvene fragment as the molecule passes to the first excited state. The effect of phenyl and styryl substituents on this transition consists in the fact that they increase its energy markedly by interacting primarily with the UOMO; because of the small contribution of the substituents, the LVMO changes slightly.

EXPERIMENTAL

The absorption spectra of solutions of the compounds in tetrahydrofuran (THF) were recorded with a Unicam SP-500 spectrophotometer. Compounds IV-XI and XVI-XXVII were previously synthesized in [10-12].

2-Phenyl-1-acetylbenzo[b]cyclopenta[e]pyran (XII). A 4-ml sample of $POCl_3$ was added dropwise with cooling and vigorous stirring to a solution of 1.22 g (5 mmole) of 2-phenylbenzo[b]cyclopenta[e]pyran I in 100 ml of dimethylacetamide (DMA). After 20 min, the reaction mixture was treated with 500 ml of hot water containing 4 g of NaOH, and the aqueous mixture was extracted with 100 ml of benzene. The extract was chromatographed with a column filled with silica gel, and the dark-red eluate was evaporated. The residue was crystallized from chloroform—heptane to give 0.94 g (65%) of red plates of XII with mp 115-117°C and R_f 0.24 [toluene—ether (4:1)].* Found: C 84.2; H 4.9%. $C_{20}H_{14}O_2$. Calculated: C 83.9; H 4.9%.

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*Here and subsequently, on Silufol UV-254 plates.

1,2-Diphenyl-3-acetylbenzo[b]cyclopenta[e]pyran (XIII). This compound, with mp 227-228°C (from n-propyl alcohol) and R_f 0.68 [acetone—toluene (1:2)], was obtained in 45% yield by acetylation of 1,2-diphenylbenzo[b]cyclopenta[e]pyran (II) at 100°C by a similar method. Found: C 86.5; H 5.3%. $C_{26}H_{18}O_2$. Calculated: C 86.2; H 5.0%.

2-Phenyl-1,3-dibromobenzo[b]cyclopenta[e]pyran (XIV). A mixture of 1.22 g (5 mmole) of 2-phenylbenzo[b]cyclopenta[e]pyran (I), 1.78 g (10 mmole) of N-bromosuccinimide, and 50 ml of benzene was stirred in the cold for 10 min, after which it was filtered, and the filtrate was diluted with heptane and chromatographed with a column filled with silica gel. The solvent was removed by evaporation, and the residue was crystallized from heptane to give 1.6 g (80%) of XIV with mp 120-123°C and R_f 0.62 [toluene—heptane (1:1)]. Found: C 53.7; H 2.6; Br 39.8%. $C_{18}H_{10}Br_2O$. Calculated: C 53.8; H 2.5; Br 39.7%.

1,2-Diphenyl-3-thiocyanatobenzo[b]cyclopenta[e]pyran (XV). A 1.28-g (4 mmole) sample of 1,2-diphenylbenzo[b]cyclopenta[e]pyran (II) was dissolved in 60 ml of acetonitrile, and 5.0 g of $Cu(SCN)_2$ was added with vigorous stirring in the course of 15 min without heating. The mixture was then diluted with 150 ml of benzene and filtered, and the filtrate was washed with warm water (three 200-ml portions). It was then dried with magnesium sulfate and chromatographed with a column filled with silica gel. The red-brown eluate was evaporated, and the residue was crystallized from benzene to give 0.9 g (60%) of brown needles of XV with mp 195-197°C and R_f 0.36 [heptane—ether (2:1)]. Found: C 79.6; H 4.1; N 3.6%. $C_{25}H_{15}NOS$. Calculated: C 79.5; H 4.0; N 3.7%.

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