

ABSORPTION, LUMINESCENCE AND POLARIZATION ELECTRONIC SPECTRA OF SOME PHENALENONE TYPE COMPOUNDS*

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Electronic absorption, fluorescence and polarization spectra have been measured in the series of phenalenones. The experimental data have been correlated with the theoretical characteristics obtained by the PPP method. The relations between structure and absorption spectra of the title compound have been studied.

Formation of phthaloylcarbazoles represents one of the most important reaction in dyestuff chemistry. Recently we studied this reaction with aminoanthraquinone derivatives¹. In that connection it was found that, on treatment with acid cyclization agents, 1-phenylaminoanthraquinone (*I*) and some of its derivatives gave predominantly coeramidonine (*II*) derivatives, whereas phthaloylcarbazole derivatives were formed only in special cases depending on the reaction conditions and structure of the starting amine. Mechanism of this dehydration ring closure was described elsewhere².

The present paper gives the results of a theoretical and experimental study of electronic spectra of some compounds of phenalenone type structurally close to coeramidonine.

EXPERIMENTAL

The substances investigated were the same as those in the report by Arient and Slavík³. Absorption spectra were measured with the use of a Unicam SP 700 apparatus equipped with a device for measuring at low temperatures⁴. Luminescence and polarization luminescence were measured with a spectrophotometer Hitachi Perkin-Elmer MPF-2A at 77 K. The luminescence spectra are not corrected. The measurements were carried out in 96% ethanol except for the B-benzocoeramidonine which was measured in 2-methyltetrahydrofuran (solubility reasons). The solvents for spectral purposes were purified in usual way.

THEORETICAL

The spectral characteristics given below in the text, π -electron bond orders and π -electron densities were calculated by the semi-empirical method LCI SCF ASMO in the

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classic PPP version⁵⁻⁷. Most of the results given were obtained in the approximation of ideal geometry (calculation with constant $\beta_{\mu\nu}^{core}$ and γ), although, with respect to the exocyclic C=O bond and angular annelation of benzene ring, the corresponding calculations with quasireal geometry approximation with variable β^{core} and γ were carried out, too. However, this paper does not give the calculation results of the latter approximation, because the final effect was not substantial, and, in addition to it, the approximation led to an unsatisfactory hypsochromic shift of the $S_0 \rightarrow S_n$ transition energies calculated with the same parametrization (situation similar to that of linear 1,4-quinones⁴).

All the four phenalenone molecules and their aza-analogues were considered to have regular ideal geometry of all the six-membered rings, all angles being 120° and all C—C and C—N bond lengths being 1.40 Å; the C=O bond length was taken 1.20 Å in accord with the experimental data⁸. The two-centers *core* integrals were calculated from simple Eq. (1)

$$\beta_{\mu\nu}^{core} = b\beta_{\mu\nu}^0, \quad (1)$$

where $\beta_{\mu\nu}^0$ was equal to -2.318 eV, and the b value for C—C and C—N bonds was taken in accord with the given bond length 1.0. A parameter study was carried out for the b value of C=O bond: the value 0.8 turned out the most suitable, being considerably different from that found for polynuclear quinones⁹ (1.1) which proved well applicable in ideal geometry approximation of linear 1,4-quinones⁴. Monocentric repulsion integrals $\gamma_{\mu\mu}$ were calculated according to Pariser approximation¹⁰ Eq. (2)

$$\gamma_{\mu\mu} = I_{\mu} - A_{\mu}, \quad (2)$$

where I_{μ} and A_{μ} are the ionization potential and electron affinity, respectively, of the atom μ in the corresponding valence state. Two-center repulsion integrals $\gamma_{\mu\nu}$ ($\mu \neq \nu$) were calculated according to Nishimoto and Mataga approximation¹¹. The mono-excited configurations involved in the calculation by the method of limited configuration interaction were produced between the four highest occupied and the four lowest virtual SCF molecular orbitals. The following parameters were used: for C⁺ *core* $I = 11.42$ eV, $A = 0.58$ eV; for N⁺ *core* (pyridine type) $I = 14.10$ eV, $A = 1.80$ eV; for C—C and C—N bond $b = 1.0$ (Eq. (1)); for O⁺ *core* $I = 13.60$ eV, $A = 2.30$ eV; for C=O bond $b = 0.8$ (from results of the parameter study); all the core charges were unity and $\beta_{\mu\nu}^0 = -2.318$ eV.

The calculations in quasireal geometry approximation respecting the alternation of the bond lengths of the carbon skeleton (especially near the exocyclic C=O bond and at the place of angular annelation of the benzene ring) were carried out with the formulas for calculation of two-centre core integrals $\beta_{\mu\nu}^{core}$ and bond length between

the vicinal atoms (repeatedly in every iteration step) given in ref.⁴ along with the following exponents of the Slater $2p_z$ atomic orbitals: 3.25 and 3.90. In every iteration step only those bonds are repeatedly calculated, the length of which was given $\sim 1.40 \text{ \AA}$ (C—C and C—N bonds in our case); the calculation did not involve any variation of the value $\beta_{\text{C=O}}^{\text{core}}$; the input C=O bond length value was 1.20 \AA . Therefore, the $\beta_{\text{C=O}}^{\text{core}}$ value was constant and identical in the both approximations.

RESULTS

Benzanthrone. Benzanthrone represents the basic compound of the series studied. Its absorption and fluorescence spectra were published before^{1,2} along with the corresponding PPP calculations. The absorption, fluorescence and APF spectra show only two absorption bands corresponding to electronic transitions in the region 23000 to 30000 cm^{-1} (Fig. 1). The first band is mirror-symmetrical to the fluorescence spectrum. The second band is less intensive and considerably overlapped by the first one: in fact it represents only a deformation of the short-wave downward section of the first band. The theoretical prediction of position and intensity of the both

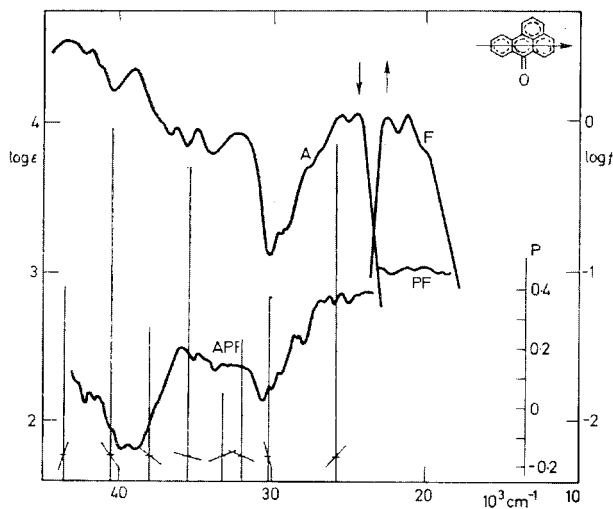


FIG. 1

Absorption, Fluorescence and Polarization Electronic Spectra of Benzanthrone in 96% Ethanol at 93 K

Arrows denote the regions of excitation and fluorescence measurements for obtaining the APF and PF spectra. Vertical lines represent the theoretical transitions obtained by the PPP method in approximation of constant $\beta_{\mu\nu}^{\text{core}}$ and $\gamma_{\mu\nu}$; the directions of individual transition moments are denoted with short lines.

bands agrees well with experiments. In the region 30000 to 37000 cm^{-1} there should be, according to the theory, several transitions with almost the same direction of polarization. The character of APF curve agrees therewith. There is a very intensive band at 39000 cm^{-1} with negative polarization degree. This band is well predicted by theory. Above the region 40000 cm^{-1} the APF curve shows an increasing trend indicating the presence of a further band in this region.

Coeramidonine. Compared to benzanthrone the absorption spectrum of coeramidonine (Fig. 2) has its first two absorption bands (with distinct vibrational structure) well separated. From the APF curve it is obvious that the both bands differ considerably in polarization direction. The position of the first band is well predicted by theory, whereas that of the second one is not, being located at somewhat higher energies than those found experimentally. Also the mutual relation of transition probabilities and transition moments directions agree with experiment. The character of the curve in the region 32000 cm^{-1} indicates the possibility of further electronic transitions in this region. The corresponding bands of the absorption curve are less perceptible. In the region 35000 to 42000 cm^{-1} the APF curve has a practically constant negative value of polarization degree. Therefrom it can be deduced that this region contains one band or several bands of approximately parallel polarization which have, however, opposite polarization with respect to the first absorption band. The theory predicts here three transitions of practically parallel polarization,

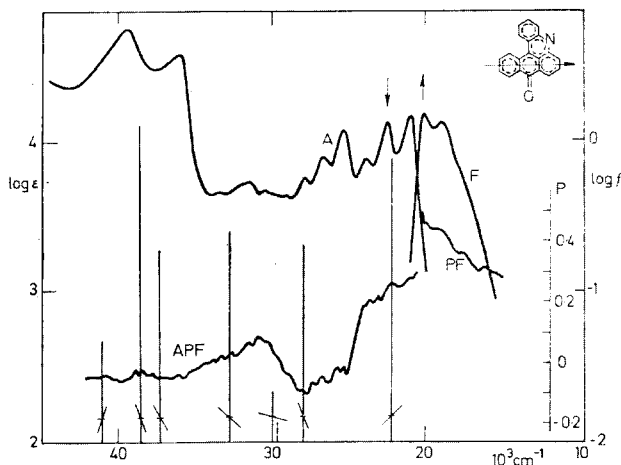


FIG. 2

Coeramidonine

For caption see Fig. 1.

which stands in good accord with experiment. Coeramidonine exhibits a very intensive fluorescence, its spectrum being mirror-symmetrical with respect to the first absorption band.

B-Benzocoeramidonine. Electronic spectrum of this compound is given in Fig. 3. From the APF curve it can be deduced that in the region 20000 to 27000 cm^{-1} there are two considerably overlapped differently polarized absorption bands. Theoretically predicted spectral characteristics agree well with experiment. The APF curve is rather inexpressive in the region 27000 to 40000 cm^{-1} , the interpretation of the further bands being thus impossible. B-Benzocoeramidonine exhibits only a weak fluorescence, its spectrum being mirror-symmetrical to the first absorption band. Phosphorescence was not observed with any of the compounds mentioned.

DISCUSSION

Phenalenone systems are interesting from the dyestuff chemist's point of view. That is why we studied theoretically five further systems besides the three abovementioned compounds, the purpose being a description of relations between electronic structure and electronic spectra of this class of compounds. Much attention was given to the exocyclic carbonyl bond. In the case of benzanthrone we carried out a parameter study for this group, concerning the ionization potential and electron affinity

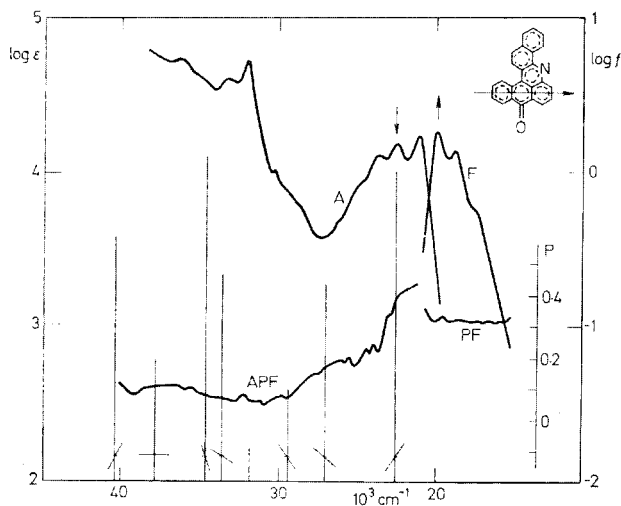


FIG. 3

B-Benzocoeramidonine

2-Methyltetrahydrofuran as solvent; otherwise as in Fig. 1.

of oxygen atom and the value of the resonance core integral resp. value of the constant in Eq. (1). We have found that the excitation energy of the first eight transitions depends only slightly on the ionization potential and electron affinity in the ranges of I_0 and A_0 values 13.60 to 17.70 eV and 2.30 to 2.50 eV, respectively. The values

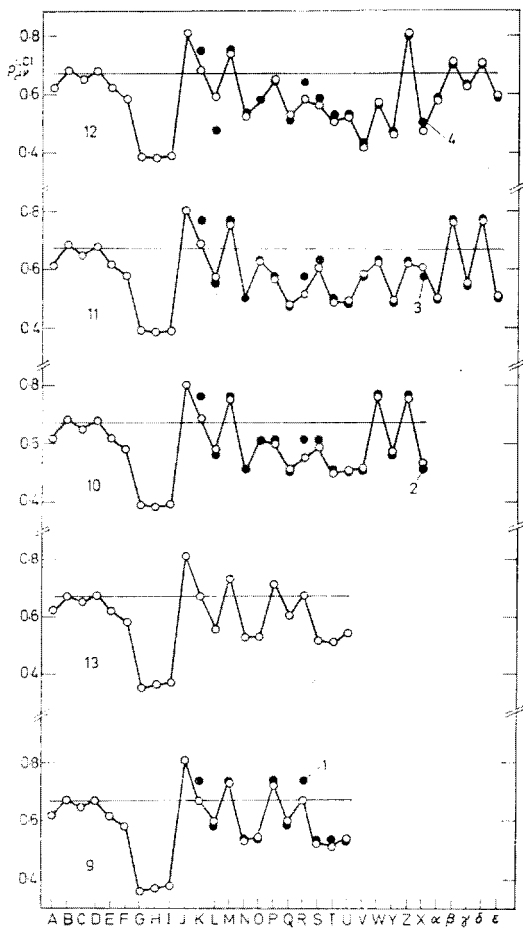


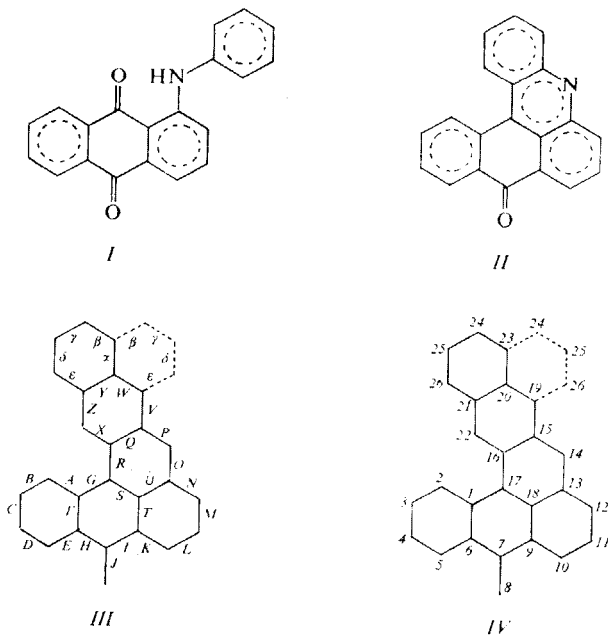
FIG. 4

Dependence of π -Electron Bond Orders $p_{\mu\nu}^{LCI}$ of Ground State on Position of Bonds in Molecules 9, 13, 10, 11, 12 resp. 1, 2, 3, 4

For notation see Scheme III, system notation see Table I; $p_{\mu\nu}^{LCI}$ for phenalene molecules resp. azabenzanthrone (○), $p_{\mu\nu}^{LCI}$ for the corresponding benzenoid hydrocarbons (1,2,3,4) calculated by PPP method for constant $\beta_{\mu\nu}^{core}$ and $\gamma_{\mu\nu}$ (●).

$I_0 = 13.60$ eV and $A_0 = 2.30$ eV were chosen for further calculation. However, dependence of the excitation energies on the parameter b is far more expressive. Dependence of SCF energy levels on ionization potential and electron affinity in the range given and that on the parameter b are also small and no crossing of levels occurs in any case. Dependence of bond orders of benzanthrone molecule in the ground state on the parameter b was investigated (calculation in the ideal geometry approximation). Four groups of bonds can be discerned: relatively single bonds G, I, H , relatively double bonds M, P exocyclic carbonyl double bond (J) and a large group of bonds of the carbon skeleton which are mainly rather more single than the bond in benzene. It is remarkable that the bonds of the benzanthrone peri-condensed system are very slightly sensitive to a change of the parameter b ; strong dependence of C=O double bond (J) on this parameter is quite understandable. Whereas the bond order value of the exocyclic C=O bond (J) considerably increases with increasing b value, the opposite is true for the adjacent considerably single bonds H, I . The single-bond-character of the "biphenyl" bond G is caused by *peri*-condensation of a benzene ring to the S and U bonds of anthracene skeleton.

Figs 4 and 5 give graphical representations of π -electron bond orders and π -electron densities of individual centres of the ground states of benzanthrone, azabenzanthrone and their benzo-analogues derived by joining a benzene ring. From the graphs it is obvious that the exocyclic C=O bond, having a clean-cut double bond character,



and the biphenyl type bond *G* cause considerable interruption of conjugation in the *peri*-adjoining skeleton. Comparison of bond orders of the hydrocarbon sections thus formed in phenalenone molecule with those of the corresponding polynuclear hydrocarbons (benzene, naphthalene, anthracene, tetracene, and 1,2-benzanthracene)

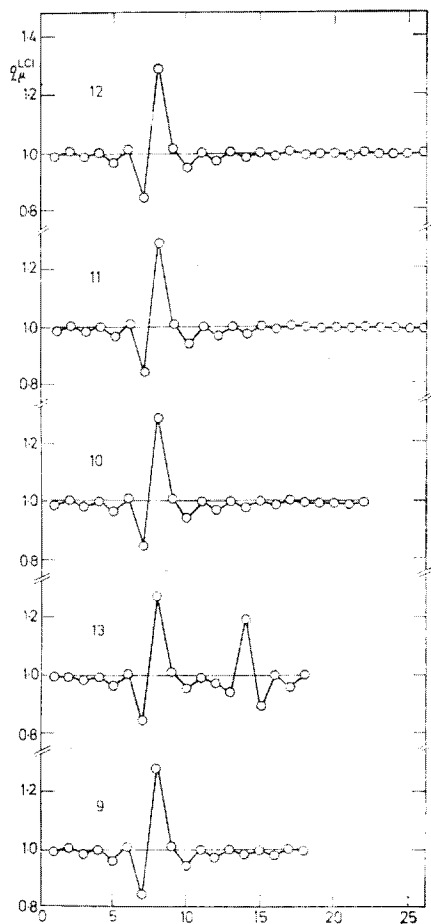


FIG. 5

Dependence of π -Electron Densities q_{μ}^{LCI} of Ground State on Position of Centres in Molecules 9, 13, 10, 11, 12

For notation see Scheme IV, system notation see Table I.

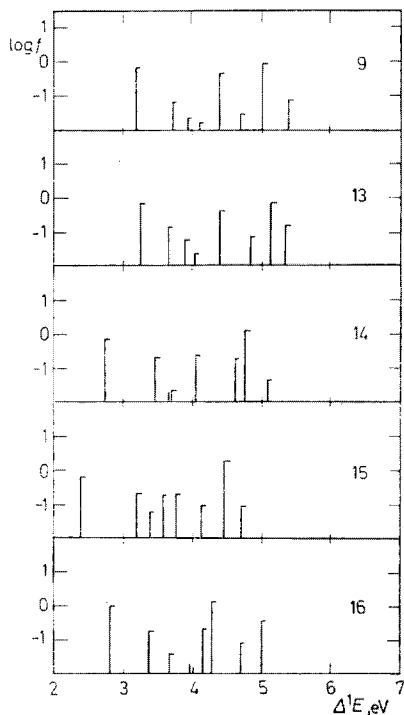


FIG. 6

Dependence of Singlet Theoretical Spectrum on Substitution by Pyridine Nitrogen (9 \rightarrow 13) and on Benzene Ring Joining Type in Molecules 9, 14, 15, 16

Notation of systems see Table I.

TABLE I
Experimental and Theoretical Data Ascribed to *p* (*para*) Absorption Band of the Studied Molecules

No ^a	Molecule	Experimental data			Theoretical data			
		$\Delta E_{\text{exp}} \cdot 10^{-3}$ cm ⁻¹	Note ^b	Ref.	$\Delta^1 E \cdot 10^{-3}$ cm ⁻¹	Main conf.	log <i>f</i>	θ^c
9	Benzanthrone	24.5	0-0	—	25.81	1,1' (94.7)	-0.16	48°
1	Naphthalene	36.4	—	14	35.07	1,1' (92.9)	-0.62	30°
13	Azabenzanthrone	—	—	—	26.27	1,1' (94.8)	-0.15	46°
5	Quinoline	35.5	—	15, 16	—	—	—	—
10	Coeranthrone	—	—	—	21.66	1,1' (97.2)	-0.12	48°
2	Anthracene	26.7	0-0	17	27.38	1,1' (96.3)	-0.52	30°
14	Coeramidonine	21.0	0-0	—	22.13	1,1' (97.6)	-0.12	46°
6	Acridine	26.4	sh	18, 19	—	—	—	—
11	A-Benzocoeranthrone	—	—	—	19.22	1,1' (98.0)	-0.12	48°
3	Tetracene	21.2	0-0	20	22.93	1,1' (97.9)	-0.43	30°
15	A-Benzocoeramidonine	—	—	—	19.16	1,1' (97.9)	-0.18	46°
7	2,3-Benzoacridine	21.5	—	19, 21	—	—	—	—
12	B-Benzocoeranthrone	—	—	—	22.48	1,1' (97.7)	-0.01	58°
4	1,2-Benzoanthracene	29.3	—	22	28.80	1,1' (95.3)	-0.36	64°
16	B-Benzocoeramidonine	21.1	0-0	—	22.70	1,1' (97.6)	0.01	59°
8	3,4-Benzoacridine	29-30	?	23	—	—	—	—

^a The numbers correspond to the numbering in Fig. 7. ^b Franck-Condon maxima are given; the note gives symbol 0-0 in cases when this transition is also an 0-0 transition. ^c Angle between the positive direction of *x*-axis and the transition moment vector; in all cases the *x*-axis is parallel with the longer axis of anthracene skeleton of benzanthrone molecule as the basic system.

indicates that molecules of phenalenones and their aza-analogues represent, from the π -electron point of view, relatively slightly interacting systems of somewhat disturbed benzene, carbonyl group and little disturbed polynuclear hydrocarbon or its aza-analogue. Comparison of benzanthrone and azabenzanthrone (Fig. 4) indicates that substitution of carbon atom by pyridine nitrogen does not affect geometry of the system, whereas from Fig. 5 one can see a significant redistribution of π -electron charge practically in the whole molecule, especially in the respective *kata*-condensed polynuclear section, due obviously to higher electronegativity of the heteroatom. Fig. 5 indicates that the disturbance inferred into the system by carbonyl group is rapidly fading with increasing distance, which is manifested by rapid decrease of charge alternation to give finally its uniform distribution characteristic for alternating hydrocarbons. In the case of aza-analogues the heterocyclic nitrogen atom represents a further site of significant disturbance. Fig. 6 gives a graphical comparison of theoretical spectra of benzanthrone, azabenzanthrone, and further three aza-analogues of phenalenones. It can be seen that the change from phenalenone to its aza-analogue is connected with a slight hypsochromic shift of the first transition in the spectrum. Also the other transitions exhibit very little shifts partly hypsochromic and partly bathochromic. Linear ring joining causes a marked bathochromic shift of theoretical spectrum as a whole, the shift of the first band (which corresponds to a very clean transition with the predominant monoexcited configuration 1,1') is very much marked. Angular ring joining, however, results in a perceptible hypsochromic shift of the first band both in the phenalenone series and its aza-analogues. The behaviour of the first singlet transition of phenalenone molecules and their aza-analogues related to joining of benzene ring is very similar to that of *p* (*para*)

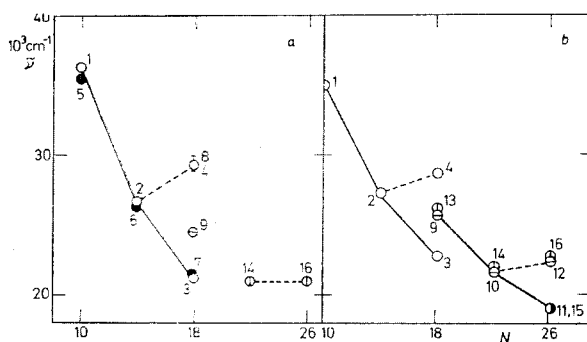


FIG. 7

Dependence of Franck-Condon Maxima of First Intensive Absorption Bands (a) and Theoretic Singlet Transitions Ascribed thereto (b) on Number (N) of Atoms in Conjugation

For notation of systems see Table I.

band resp. the corresponding singlet transition of *kata*-condensed benzenoid hydrocarbons¹³. This analogy along with the presence of bonds with considerably single bond character (*G, H, I*) made us to compare spectral characteristics of the first singlet band resp. transition of the phenalenone molecules and their aza-analogues with *p* bands of the corresponding benzenoid hydrocarbons and their aza-analogues. Table I gives the spectral characteristics of the first singlet transition of the studied phenalenones and their aza-analogues along with those of *p* bands of the corresponding benzenoid hydrocarbons and their aza-analogues. Theoretical data of this Table are only our own consistent theoretical results obtained by PPP method. The singlet transition ascribed to the experimental maximum corresponds to $S_0 \rightarrow S_1$ transition in the case of all the molecules studied. Dependence of energy of *p* band on the type of ring joining of benzene nucleus in the case of phenalenones and their aza-analogues has a similar character with the ring joining graphs for *p* band of *kata*-condensed benzenoid hydrocarbons and their aza-analogues (Fig. 7). (Numerical values of the spectral characteristics obtained by the PPP method in the both approximations are available in the authors' laboratories.)

REFERENCES

1. Arient J., Slavík V., Marhan J.: Chem. listy 60, 1509 (1966).
2. Arient J., Slavík V., Kratochvíl V., Nepraš M.: This Journal 36, 2005 (1971).
3. Arient J., Slavík V.: This Journal 34, 3576 (1969).
4. Novák A., Titz M., Nepraš M.: This Journal 39, 1532 (1974).
5. Pariser R., Parr R. G.: J. Chem. Phys. 21, 466, 767 (1953).
6. Pople J. A.: Trans. Faraday Soc. 49, 1375 (1953).
7. Parr R. G. in the book: *Quantum Theory of Molecular Electronic Structure*. Benjamin, New York 1964.
8. Trotter J.: Acta Cryst. 13, 86 (1960).
9. Titz M., Nepraš M.: This Journal 37, 2674 (1972).
10. Pariser R.: J. Chem. Phys. 21, 568 (1953).
11. Nishimoto K., Mataga N.: Z. Physik. Chem. (Frankfurt) 12, 335; 13, 140 (1957).
12. Zahradník R., Tichý M.: Tetrahedron 24, 3001 (1968).
13. Koutecký J., Hochmann P., Titz M.: J. Phys. Chem. 70, 2768 (1966).
14. UV-Atlas Organischer Verbindungen, Vol. 2; E 1/1. Verlag Chemie, Weinheim 1966.
15. UV-Atlas Organischer Verbindungen, Vol. 3; H 1/1. Verlag Chemie, Weinheim 1966.
16. Zimmermann H., Joop N.: Z. Elektrochem. Ber. Bunsenges. Physik. Chem. 65, 61 (1961).
17. UV-Atlas Organischer Verbindungen, Vol. 2; E 2/1. Verlag Chemie, Weinheim 1966.
18. UV-Atlas Organischer Verbindungen, Vol. 3; H 8/1. Verlag Chemie, Weinheim 1966.
19. Zanker V., Schmid W.: Chem. Ber. 90, 2253 (1957).
20. UV-Atlas Organischer Verbindungen, Vol. 2; E 4/2. Verlag Chemie, Weinheim 1966.
21. UV-Atlas Organischer Verbindungen, Vol. 3; H 8/35. Verlag Chemie, Weinheim 1966.
22. UV-Atlas Organischer Verbindungen, Vol. 2; E 5/3. Verlag Chemie, Weinheim 1966.
23. Zanker V., Schmid P.: Chem. Ber. 92, 615 (1959).

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