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PHYSICAL PROPERTIES AND CHEMICAL REACTIVITY OF ALTERNANT HYDROCARBONS AND RELATED COMPOUNDS—XIV[1]

BASICITY AND ELECTRONIC SPECTRA OF PHENALENONES

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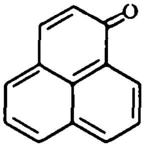
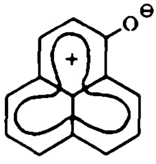
Abstract— The absorption and fluorescence electronic spectra of a number of phenalenones have been measured. The spectrophotometric method was employed for determining pK_{BH^+} values in a solution of $HClO_4$ in dioxan. The basicity of phenalenones in the first singlet excited states was estimated by means of the Förster cycle. The experimental results are discussed in terms of the HMO, SCF and LCI-SCF methods.

THE fundamental representative of this group of compounds, phenalenone (Ia), can be formally derived by a combination of the phenalenium cation with the oxygen anion (Ib). Structure Ib reflects the various properties of phenalenone (high basicity, high dipole moment, IR spectrum). In an acid medium, phenalenone behaves as a conjugate acid of the form Ib, i.e. as a hydroxy derivative of the phenalenium cation. The $2p_z$ atomic orbital of oxygen contributes to the conjugation by one π-electron in the form Ia and by two π-electrons in the form Ib.


Ia


Ib

The synthesis of phenalenones, some of their properties and their occurrence among natural substances have recently been subjected to a comprehensive treatment.[2] We now report an experimental and theoretical study of the substances I–IX.

THEORETICAL

The usual version of the Pariser–Parr–Pople LCI–SCF method[3] has been employed. Interaction among sixteen monoexcited configurations (formed by the excitation

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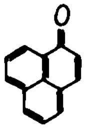

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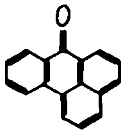

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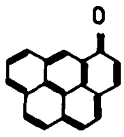

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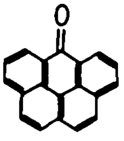

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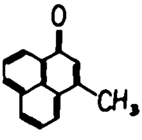

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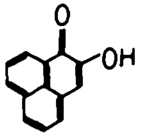

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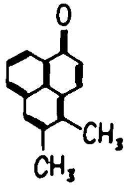

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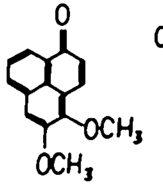

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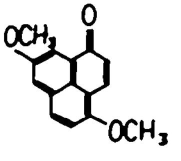

IX

of one π-electron from the four highest occupied MO's into the four lowest unoccupied MO's) has been considered. The following parameters (in eV) were used:

Atom μ	I_μ	A_μ	$\gamma_{\mu\mu}$	Z_μ	$\beta_{C-\mu}$	$l_{\mu\nu}$ (Å)
C	11·22	0·69	10·53	1	−2·388	1·4
O(in C=O)	13·6	2·3	11·3	1	−2·388	1·2
O(in C—OH)	32·9	10·0	22·9	2	−1·433	1·4

I_μ and A_μ represent the ionization potential and electron affinity, $\gamma_{\mu\mu}$ is the monocentric electronic repulsion integral, $\beta_{C-\mu}$ is the core resonance integral, and $l_{\mu\nu}$ denotes the bond length. The bicentric electronic repulsion integrals have been calculated by the Mataga–Nishimoto formula[4]

$$\gamma_{\mu\nu} = \frac{14 \cdot 399}{R_{\mu\nu} + 1 \cdot 328}\,\text{eV}$$

where $R_{\mu\nu}$ (Å) is the distance between atoms μ and ν.

The same set of parameters has been used for the calculation of bond orders and π-electron densities by the Pople SCF procedure[3] (in the text and tables denoted by the index SCF).[*]

HMO calculations were carried out by means of the following empirical parameters:

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[*] For details see Ref. 5.

Atom (group) μ	δ_μ	$\delta_{(\mu)}$	$\beta_{C\mu}$
$=$O(in CO)	1·3	0·2	2
$=$O(in C –OH and in C –OCH_3)	2	0	1
$-$C(in CH_3)	0	$-$0·1	0·8
$\equiv H_3$(in $C-CH_3$)	$-$0·5	0	3·0

The quantities δ_μ and $\beta_{\mu\nu}$ are defined by the following equations:

$$\alpha_X = \alpha + \delta_X \beta \tag{1}$$

$$\beta_{XY} = \rho_{XY} \beta \tag{2}$$

where α_X and β_{XY} are the Coulomb and the resonance integral of the HMO method.[6]

Various HMO and LCI–SCF quantities including molecular diagram calculated by the SCF method are available on request at the authors.

RESULTS AND DISCUSSION

Basicity of phenalenones

The quantum-chemical interpretation of the equilibrium data is simpler than that of the kinetic data, because the structure of the initial substances and of the products is relatively well known, which is not the case as regards the rate processes (where the pair initial substance-activated complex is involved). In the π-electron approximation, on the assumption that a parallelism exists between the changes of enthalpy and entropy accompanying the dissociation and on other known assumptions,[7] it is possible to estimate the logarithms of the dissociation constants (pK_a values) from the differences of the π-electron energy of the free base and of the conjugate acid. In our case, the following equation is involved:

$$P = \overset{+}{O}H \rightleftharpoons P = O + H^+ \tag{3}$$

In Eq. 3, P = O denotes phenalenone and its derivatives (free base), and $P = \overset{+}{O}H$ is the conjugate acid.

Table 1 presents the experimentally determined values of pK_{BH^+} together with the MO characteristics. Besides the parallelism between pK_{BH^+} and ΔW (Fig. 1), a parallelism between pK_{BH^+} and the π-electron density on oxygen exists for phenalenones similar to that for amines and heterocycles of the pyridine type:

$$pK_{BH^+} = 27{\cdot}78\,\Delta W - 16{\cdot}80, \quad r = 0{\cdot}929, \quad \sigma(pK) = \pm 0{\cdot}32, \quad n = 9 \tag{4}$$

$$pK_{BH^+} = 31{\cdot}67\,q_0 - 49{\cdot}68, \quad r = 0{\cdot}955, \quad \sigma(pK) = \pm 0{\cdot}26, \quad n = 9 \tag{5}$$

where r denotes the correlation coefficient, n is the number of substances, and $\sigma(pK)$ is the standard deviation from the regression line. The values of r correspond to close correlations.

When going through Fig. 1 more carefully, it can be seen, however, that there is a splitting of data into two groups according to the type of the position, in which the O atom is bound (α-naphthalene type—class 1, mesoanthracene type—class 2). Evidently, this is an analogous splitting of data as that observed in the case of the

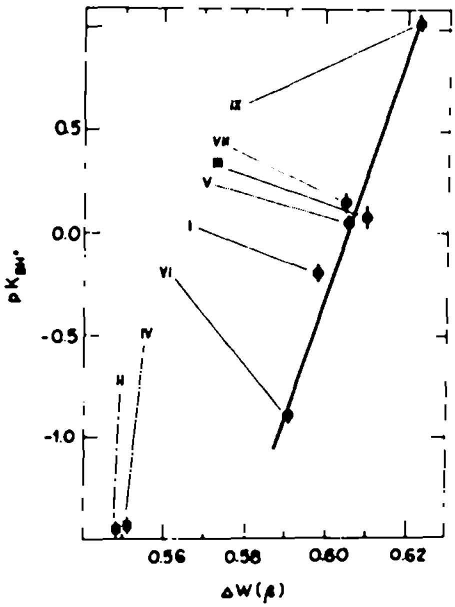

Fig. 1 Plot of pK_{BH^+} against ΔW for phenalenones. Full line respects differentiation of data according to classes[8] (● position of class 1, ■ position of class 2). Abscissae indicate magnitude of measuring errors.

protonation of benzenoid hydrocarbons as well as in the case of various electrophilic substitutions.[8,9] It has been shown that the splitting is due to the neglect of the electronic repulsion in the HMO method.

The interrelation between the pK_{BH^+} values and the MO characteristics for a series of carbonyl compounds of different structural types was studied by Kende,[10] who showed that the correlation is much closer with the use of the SCF energies than with that of the HMO energies. This is understandable in view of the diversity of the structural types investigated by this author.

In Table 2 are summarized the values of $pK^*_{BH^+}$ as calculated from the absorption and the fluorescence spectra of phenalenones. The values calculated by various methods differ from one another; however, qualitatively it can be said that the phenalenones in the first excited singlet state are essentially stronger bases than in the ground state. The increase in basicity is highest for the ketones II and IV, and the value of ΔpK_{BH^+} is somewhat lower for the ketones I and III.

Analogously to the possibility of correlating the pK_{BH^+} values of phenalenones in the ground state with the ΔW and the q_0 values, we endeavoured to predict by means of the HMO method also the relative basicity in the first excited state on the assumption that the excitation is connected with the transition of the π-electron from the highest occupied to the lowest unoccupied MO. (It will be shown later that this assumption is justified except in the case of the protonated form of phenalenone.)

Since the change of the pK_{BH^+} values in the transition from the ground state to the excited state has been estimated by means of the Förster cycle,[11–13] it appears possible to estimate ΔpK_{BH^+} by means of the difference of the values $E(N \rightarrow V_1)$ of the base and the conjugate acid, $\Delta E(N \rightarrow V_1)$. Although the parallelism between ΔpK_{BH^+} and $\Delta E(N \rightarrow V_1)$ is not close, it is nevertheless worth mentioning. The correlation is not improved by replacing the HMO excitation energies by the LCI excitation energies. The calculated $pK^*_{BH^+}$ can also be roughly estimated by means of the difference between the HMO π-electron energies of the base and the conjugated acid in the first excited state (ΔW^*). As in the ground state, there exists also in the $N \rightarrow V_1$ excited state a linear dependence between the change of the π-electron energy accompanying the transition from the free base to the conjugate acid and the π-electron density on the O atom in the free base.

Electronic spectra

Absorption and fluorescence curves of four principal phenalenones are presented together with the results of the calculation of the spectral characteristics by the LCI–SCF method in Fig. 2 (free bases) and in Fig. 3 (conjugate acids).

Besides the LCI excitation energies, the figures show also data on the oscillator strength and on the directions of the polarization of the individual singlet-singlet transitions (the short dash lines indicate the expected position of the first $S \rightarrow T$ transition). Moreover Figs 2 and 3 present information about the weight of the individual mono-excited configurations (represented by combinations of Slater determinants) in the LCI wave functions. Since the experimental oscillator strengths are difficult to calculate, owing to considerable overlapping of bands, we have limited ourselves to an empirical coordination of the logarithms of oscillator strengths to the logarithms of the molar extinction coefficients. The following empirical relation is satisfactory for these purposes:

$$\log \varepsilon = \log f + 4. \tag{6}$$

The position of forbidden transitions ($f = 0$) is indicated by a wavy line with an arrow. The directions of polarization are marked under the symbols of the individual LCI wave functions ${}^1\phi_i$ by both-sided arrows; their direction relates to the formulae which are oriented as given in the figures. The circles under symbols of the LCI wave functions denote the weights of the individual mono-excited configurations (the indices of the configurations are given in the left part of the lower half of the figures); since the radius of these circles is equal to the expansion coefficients of the LCI wave functions, their area is proportional to the weight of the individual configurations in the functions ${}^1\phi_i$. The figures show the contributions of those configurations only which are indicated by a coefficient exceeding or equalling the value 0·33. Finally, for estimating the magnitude of the contributions there is a circle above the indices of the configurations, and its area corresponds to the 100% weight of the configuration in the respective LCI wave function.

From Figs 2 and 3 it is obvious that the agreement between the theory (LCI–SCF data) and the over-all character of the absorption curves is in general rather satisfactory. With the exception of protonated phenalenone that configuration in the wave function of the first singlet excited state always dominates which corresponds to the excitation of the electron from the highest occupied MO to the lowest unoccupied MO (in the ground state), i.e. to the $N \rightarrow V_1$ excitation of the HMO theory. (In the case of benzo[cd]pyrene-6-one, an almost equal energy is exhibited by the transitions from the ground state to the state with dominating 10 → 11 configuration

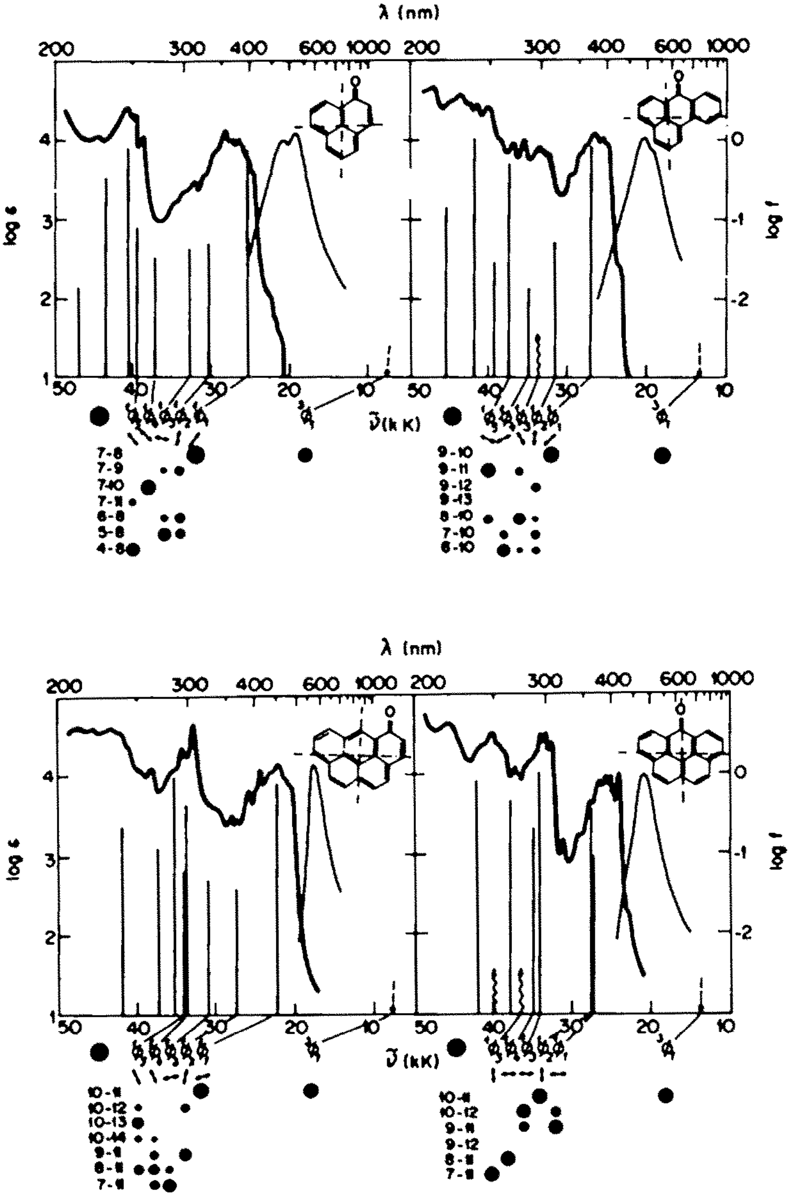

FIG. 2 Comparison of the calculated LCI-SCF spectral characteristics with the experimental absorption curves (cyclohexane) and the experimental fluoroescence spectra (40% aqueous dioxan) of phenalenones. Absorption spectra are represented by the strong, fluorescence spectra by the weak lines. For theoretical data see text.

and to the state in which the 9 → 11 and 10 → 12 configurations manifest themselves.) Despite this fact, no close correlation has been found between the wave-numbers of the first bands of absorption spectra and the energies of the $N \rightarrow V_1$ transitions; the situation is more favourable in the case of the correlation of the maxima of the

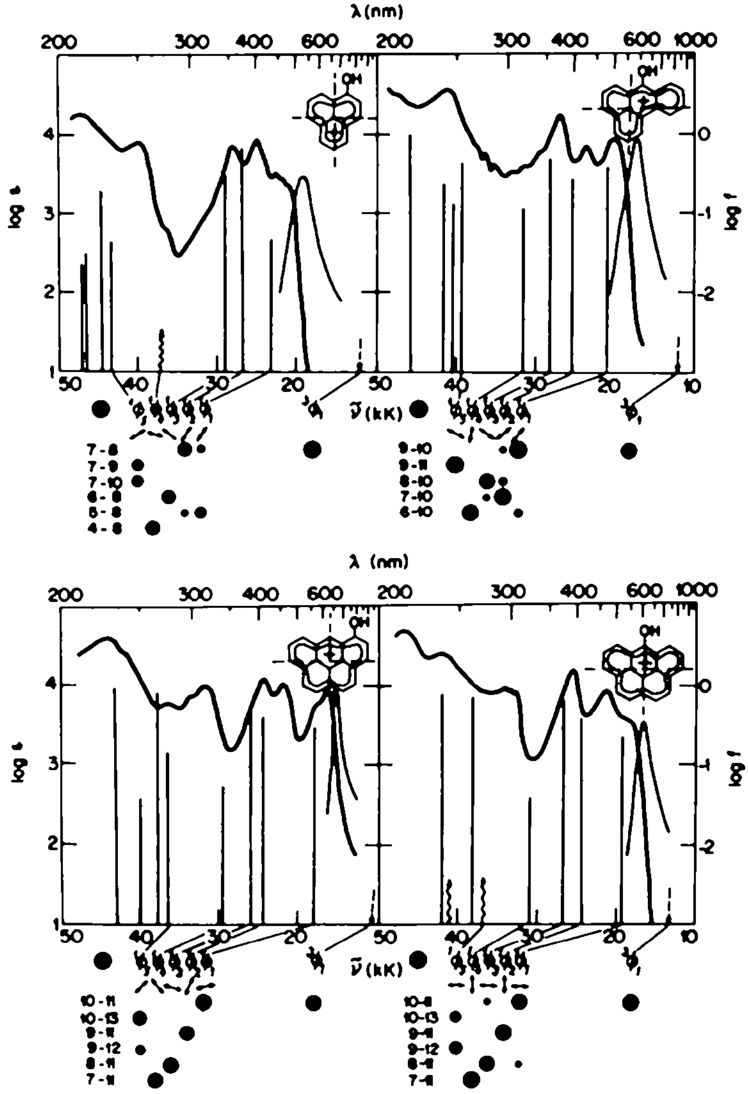

FIG. 3 Comparison of the calculated LCI-SCF spectral characteristics with the experimental absorption curves (96% H_2SO_4) and the experimental fluorescence (70% $HClO_4$ + dioxan 3:2 v/v) spectra of protonated forms of phenalenones. Absorption spectra are represented by the strong, fluorescence spectra by the weak lines. For theoretical data see text.

fluorescence curves and the intersection of the absorption and the fluorescence curve (Fig. 4).

A comparison of the positions of the first theoretical and experimental transitions shows that the theoretical values are shifted slightly hypsochromically.

The similarity between the absorption curves of the protonated forms of phenalenones and the absorption curves of phenalenium cations has been discussed in the preceding paper.[1]

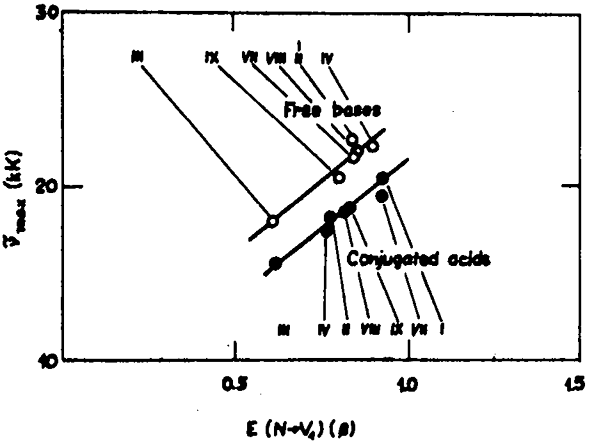

FIG. 4 Correlation of $E(N \rightarrow V_1)$ values with the wave numbers of the intersection of absorption and fluorescence spectra (○ phenalenones, ● hydroxyphenalenylium cations).

The absorption curves of phenalenones in cyclohexane exhibit in the long-wave branch of the first band a shoulder whose log ε approximately equals 2. The intensity of this band and its hypsochromic shift in the transition from cyclohexane into 40% aqueous dioxan indicate that n—π* bands are concerned.

It follows from a comparison of the SCF and the LCI–SCF excitation energies of the systems studied that the configuration interaction never causes a crossing of the energy levels at the first excited bands. Finally, it is worth mentioning that the influence of configuration interaction upon the SCF excitation energies is distinctly smaller for the protonated forms than for the free bases.

TABLE 1. pK_{BH^+} OF PHENALENONES IN 40% AQUEOUS DIOXAN AND THEORETICAL CHARACTERISTICS

Compound	pK_{BH^+}[b]	ΔW[a]	q_O	q_O^{SCF}
I	−0·19 ± 0·01	0·598	1·562	1·264
II	−1·45 ± 0·03	0·548	1·520	1·258
III	0·08 ± 0·05	0·610	1·572	1·269
IV	−1·44 ± 0·06	0·551	1·523	1·260
V	0·06 ± 0·02	0·606	1·570	—
VI	−0·89 ± 0·01	0·591	1·547	—
VII	0·15 ± 0·06	0·605	1·569	—
VIII	0·08 ± 0·02	0·621	1·586	—
IX	1·05 ± 0·02	0·623	1·588	—

[a] $\Delta W = W_{OH} - W_O$; $W_{OH(O)}$: total π-electron energy of an acid (base), q_O: π-electron density of the carbonyl oxygen atom of a base.

[b] Values calculated from the first absorption bands.

TABLE 2. p$K^*_{BH^+}$ VALUES OF PHENALENONES[a]

Compound	p$K^*_{BH^+}$				ΔW^*	q^*_O	$\Delta E(N \rightarrow V_1)$
	1	2	3	4			
I	8·8	3·2	4·4	5·9	0·515	1·477	0·083
II	6·9	5·4	7·5	6·3	0·605	1·564	−0·057
III	8·9	3·7	4·9	6·2	0·599	1·549	0·011
IV	9·5	6·2	8·5	7·8	0·674	1·646	−0·123
VII	4·4	4·2	4·8	4·2	0·523	1·483	0·082
VIII	8·1	5·8	7·9	7·0	0·665	1·509	−0·044
IX	3·4	6·1	4·7	4·7	0·597	1·532	0·026

[a] Values calculated as follows: 1 from the absorption spectra, 2 from the fluorescence spectra, 3 from the intersections of the absorption and fluorescence spectra, 4 from the arithmetic mean of the longest-wave length absorption band and the shortest-wave length fluorescence band; $\Delta W^* = W^*_{OH} - W^*_O$; $\Delta E(N \rightarrow V_1) = E_{OH}(N \rightarrow V_1) - E_O(N \rightarrow V_1)$; $E(N \rightarrow V_1)$: energy of the $N \rightarrow V_1$ transition.

EXPERIMENTAL

The pK_{BH^+} values in the solutions of perchloric acid in 40% dioxan[14] of the compounds studied both in their ground[15] and in their first excited singlet state [11–13, 16–20] have been obtained by means of the standard techniques and procedures. The electronic absorption spectra have been recorded by means of an UNICAM SP 700 double-beam recording spectrophotometer; the fluorescence spectra using an Optica Milano CF 4 NI spectrophotometer by the procedure described by Lippert *et al.*[21]

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