CHEMISTRY OF THE PHENOXAZINES

I. EFFECT OF ANNELATION ON THE ELECTRONIC STRUCTURE AND THE ELECTRONIC SPECTRA OF PHENOXAZINES

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The π-electron charges, bond orders, and energy levels of phenoxazin-3-one and eight of its mono- and diannelated derivatives were calculated by the Hückel MO LCAO method. The effect of the position of the annelated benzene ring on the electronic characteristics of the compounds was estimated. A satisfactory correlation between the experimental and calculated energies of the $\pi_1 \rightarrow \pi_1^*$ transitions was found.

Phenoxazine derivatives are of interest as potential physiologically active compounds [1] and they also have interesting properties in a theoretical respect: they fluoresce in visible and UV light [2], they display halochroism [3], and they have different colors in transmitted and reflected light. Phenoxazine dyes have special electrical and magnetic properties. Many derivatives of this series have pronounced metachromatic activity [4] and may be of interest for elucidating the fine problems of the interaction of a dissolved substance with the medium. The reactivity of phenoxazine depends substantially on the number and position of the benzene rings annelated to the phenoxazine skeleton [5, 6]. In this connection it is of interest to elucidate the effect of annelation on the electron structure, physicochemical properties, and reactivities of phenoxazines.

In this communication the effect of annelation on the electronic structure of all possible mono- and diannelated derivatives of phenoxazin-3-one is studied by the Hückel MO LCAO method. (See scheme on next page.)

The problem of the effect of annelation on the properties of aromatic and heteroaromatic compounds containing closed π-electron systems which do not lie outside the condensed nuclei has been studied by

TABLE 1. Energy Indexes and Absorption Spectra of Phenoxazinones I-IX

Comp.	E^{π}	$E^{\pi*}$ upper bonding	$E^{\pi*}$ lower antibond.	$E^{\pi_1 \rightarrow \pi_1^*}$	λ_{max}, nm		lg ε
					calc.	expt.	
I	16α+26,340β	0,515	0,183	0,698	451	442	4,108
II	20α+32,248β	0,488	0,251	0,739	427	430	4,164
III	20α+32,072β	0,438	0,191	0,629	501	486	4,269
IV	20α+32,060β	0,431	0,203	0,634	497	—	—
V	20α+32,016β	0,539	0,154	0,693	455	—	—
VI	24α+37,972β	0,409	0,262	0,671	470	482	4,348
VII	24α+37,960β	0,405	0,279	0,684	462	479	4,218
VIII	24α+37,926β	0,512	0,227	0,739	427	—	—
IX	24α+37,862β	0,409	0,212	0,621	507	—	—

*$E^{\pi}_{\text{upper bonding}}$, $E^{\pi}_{\text{lower antibonding}}$, and $E^{\pi_1 \rightarrow \pi_1^*}$ values are given in units of β.

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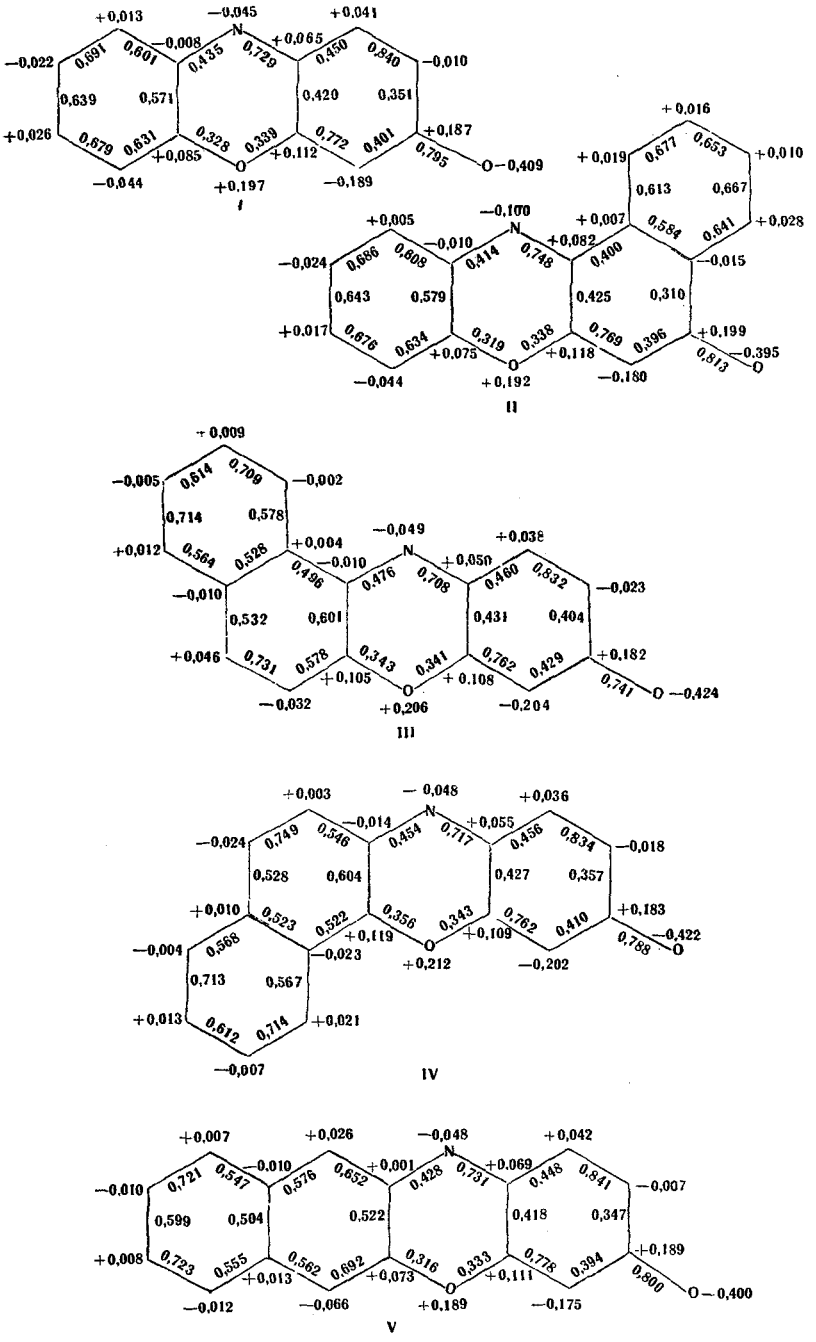
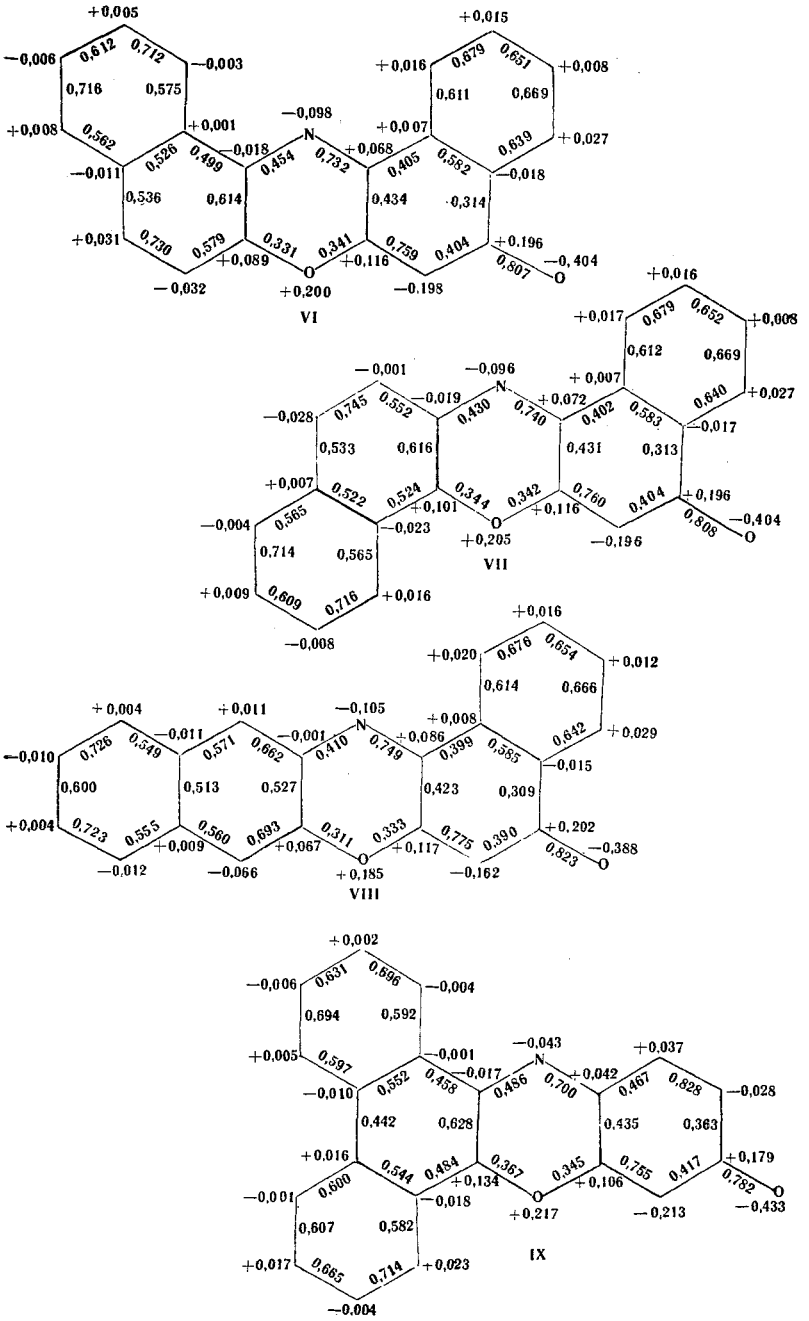


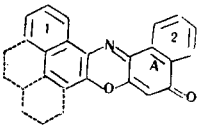
Platt [7], Brown [8], and Pullman [9]. In the examined series of phenoxazinones the π-electron system is branched due to the π electrons of the exo carbonyl group and is relatively rigidly attached to the p-quinonimine portion of the molecule.

It is apparent from a comparison of the total π-electron energies of the molecules (Table 1) that the monoannelated derivatives are arranged in the following order with respect to stability: II > III > IV > V, i.e., all the angular isomers are more stable than linear isomer V. Among the angular isomers the maximum stability is inherent in compound II in which the quinonimine portion of the phenoxazin-3-one molecule (I) is annelated. This agrees with the sharp decrease in the order of bond A in compound II as compared with order of bond A in unsubstituted I. Annelation at the benzoid moiety of the phenoxazinone molecule to form compounds III-V has virtually no affect on the order of this bond, which indicates the considerably



Molecular diagrams of phenoxazinones.

stronger delocalization of the electrons of bond A during annelation of the quinonimine moiety of phenoxazinone.



A similar phenomenon is also characteristic for the diannelated derivatives of phenoxazin-3-one: compounds VI and VII are more stable than compound VIII, in which there is a linearized ring (1) in addition to angulated ring (2). Compound VIII is in turn more stable than IX, in which both rings are annelated to the benzoid portion of the molecule; i.e., the diannelated derivatives are arranged in the order VI > VII >

TABLE 2. Interaction Energies and Total Charge of the Butadiene Fragment of Phenoxazinones II-IX

Comp.	E_{int}^{π} with respect to I-V*					Total charge of butadiene portion (function of benzene ring)	
	I	II	III	IV	V	ring condensed with the benzoid portion	ring condensed with the quinonimine portion
II	1,436						+0,073
III	1,260					+0,014	
IV	1,248					+0,023	
V	1,204					−0,007	
VI	2,688	1,252	1,428			+0,004	+0,066
VII	2,676	1,240		1,428		+0,013	+0,068
VIII	2,642	1,206			1,440	−0,014	+0,077
IX	2,568		1,318	1,330		−0,003	
						+0,035	

*The E_{int}^{π} values are given in units of β.

VIII > IX with respect to increasing E^{π}. The orders of the A bonds in these diannelated derivatives also correlate with this – they decrease abruptly only in those compounds where there is a ring (2) annelated with respect to the quinonimine portion of the molecule.

The magnitude of the interaction energy (E_{int}^{π}) [10], which is the difference between the π-electron energies of the benzo- or dibenzophenoxazinone and the phenoxazinone or benzophenoxazinone, respectively, was used to estimate the effect of each newly introduced benzene ring. In addition, the π-electron energy of one or two butadiene fragments ($4\alpha + 4.472\beta$) was subtracted from this difference since the π-electron system is enlarged by a butadiene fragment on introduction of each new benzene ring.

$$E_{int}^{\pi} = E^{\pi}_{\substack{\text{benzo-}\\(\text{dibenzo-})}} - E^{\pi}_{\substack{\text{phenoxazinone}\\(\text{benzo-})}} - nE^{\pi}_{\text{butadiene}}$$

Of the monoannelated phenoxazinone derivatives the greatest E_{int}^{π} value (Table 2) is characteristic for compound II, in which the benzene ring is condensed with the quinonimine portion of the molecule. The phenoxazinones are arranged in the above orders with respect to E_{int}^{π}.

The effect exerted by a second introduced benzene ring on the already once-annelated phenoxazin-3-one derivative can also be estimated from E_{int}^{π}. For example, VI can be considered to be the result of annelation with the benzene ring of both compound II and compound III. It is apparent from comparison of E_{int}^{π} of the second benzene ring with the monoangulated phenoxazinone molecule (1.252β for II and 1.428β for III) that the second ring has a considerably smaller effect if the first is already situated in the quinonimine moiety of the molecule, while introduction of a new ring in precisely this moiety of the molecule increases E_{int}^{π} significantly. The same picture is characteristic for all the remaining diannelated compounds. It thus follows from an examination of E^{π} and E_{int}^{π} that in the series of annelated phenoxazinones, just as in the case of benzoid systems of the anthracene and phenanthrene type [11], angulation has a greater effect on the increase in the molecular stability than linearization. However, in contrast to the latter, the effect of angulation in the case of phenoxazinones depends substantially on the position of the angulated benzene ring: the increase in the stability and E_{int}^{π} turns out to be greater for angulation of the quinonimine portion of the phenoxazinone molecules than for angulation of the benzoid portion of the same molecule.

The total π-electron charge on the butadiene fragment of each new benzene ring was determined to establish the character of the electronic effect of the benzene rings introduced (Table 2). Examination of these indexes indicated that in both the mono- and diannelated compounds, except for IX, all of the angulated benzene rings act as electron donors, while the linearized ring in compounds V and VIII acts as an electron acceptor. Moreover, the ring angulated to the quinonimine portion of the molecule is a stronger donor than that angulated to the benzoid portion of the phenoxazinone molecule. Since all the rings angulated to the quinonimine portion are stronger donors than the linearized ring is an acceptor, and since one of the benzene rings in the diannelated compounds is always angulated to the quinonimine portion, the overall effect of both rings turns out to be electron-donating. In connection with the competitive action of two annelated benzene rings in compounds VI and VII, the donor effect of ring 2 decreases somewhat in comparison with mono-

annelated compound II. Benzene ring 2 becomes the strongest donor only in the linear-angular compound VIII, while ring 1 becomes the strongest acceptor. The explanation of this fact probably involves electron transfer according to the type of coincident orientation of one donor (angulated) ring 2 to the other acceptor (linearized) ring 1. In compound IX, where both rings are angulated to the benzoid portion of the molecule, there is a significant increase in the donor activity of one ring (upper), while the other (lower) becomes a weak acceptor.

By acting as an electron donor or acceptor with respect to the phenoxazin-3-one molecule, the annelated benzene ring has a different effect on the individual fragments of the molecule in redistributing the π-electron density on them via an inductive or mesomeric mechanism. It is apparent from the molecular diagrams of the phenoxazinones (see schemes) that benzene ring 2, which is a donor with respect to the entire phenoxazin-3-one molecule, behaves as an acceptor with respect to the carbonyl group of compound II, while benzene ring 1 in compounds III and IV acts as an acceptor for the ether oxygen atom but, conversely, as a donor in compound V. The principles are similar in the case of diannelated compounds, but the final effect is the sum of the effects of two rings.

The capacity of the molecule for transfer or addition of electrons was estimated from the energies of the upper bonding and lower antibonding orbitals, respectively. All of the compounds are satisfactory electron donors and very strong acceptors in accordance with the Szent-Gyorgyi classification [12] (Table 1). The compounds are arranged in the order VII > VI = IX > IV > III > II > VIII > I > V with respect to donor capacity, while the series for the acceptor strength is almost the opposite of this: V > I > III > IV > IX > VIII > II > VI > VII, i.e., the weakest electron donors are the strongest electron acceptors. It is apparent from these orders that monoangulation decreases the acceptor properties of the molecule, while monolinearization increases them. Double angulation more strongly hinders addition of electrons, while compound VIII, which has both an angulated and a linearized ring, has average acceptor strength. Compound IX, which in a certain sense can be represented as a combination of the structures of compounds III and IV, has the strongest acceptor properties as compared with the other dibenzo derivatives, i.e., in this case, introduction of benzene rings into compounds III and IV increases the acceptor properties of the molecules.

All of the phenoxazinones studied have unshared electron pairs on the heteroatoms. However, the very high intensity of the long-wave absorption bands of compounds I-III, VI, and VII (Table 1) does not enable one to ascribe these bands to $n \rightarrow \pi^*$ transitions. Calculations of the transition energies for these five compounds indicate that the long-wave bands originate from $\pi \rightarrow \pi^*$ transitions. The β_{sp} value of 90.98 kcal/mole used to calculate λ_{max} of compounds I-IX was determined by solution of the inverse spectral problem for compounds I-III, VI, and VII and by averaging the values obtained. The satisfactory agreement between the calculated and experimental λ_{max} values for compounds I-III, VI, and VII made it possible to use the β_{sp} value found to calculated λ_{max} of compounds IV, V, VIII, and IX. From comparison of λ_{max} it can be noted that angulation of the quinonimine portion of the phenoxazin-3-one molecule (compound II) causes a hypsochromic shift of the $\pi_1 \rightarrow \pi_1^*$ transition, while angulation of the benzoid portions leads to a rather pronounced (up to 50 nm) bathochromic shift of this transition. Linearization of the benzoid portion (compound V) gives only a very slight bathochromic shift of the first absorption band. Thus, the phenoxazinones, owing to the presence of a quinonimine system, differ substantially from the benzoid hydrocarbons, where an increase in the number of linearly condensed rings leads to a most pronounced bathochromic shift of the first band. In addition, in the series of benzoid hydrocarbons one observes a hypsochromic shift on passing from linear isomers to angular isomers for systems which have an equal number of condensed rings [11], while in the phenoxazinone series only angulation of the quinonimine portion of the molecule leads to a hypsochromic shift, while angulation of the benzoid portion gives a bathochromic shift (compounds II-V). In the case of dibenzophenoxazinones the shift in the absorption maximum depends on the overall effect of two benzene rings, so that the bathochromic shift of the absorption band of compounds VI and VII is less than in the case of the corresponding monoannelated compounds III and IV. A hypsochromic shift does occur in compound VIII since the effect of benzene ring 2 is much more pronounced than the effect of linearized ring 1. The effect of both rings has the same direction only in compound IX and leads to the most pronounced bathochromic shift in the entire series.

EXPERIMENTAL

The secular determinants were solved with a "Ural-2" computer in the computer center of the S. M. Kirov Ural Polytechnical Institute from the program described in [13]. Pullman parameters [14, 15] were used in the calculations.

The absorption spectra of benzene solutions in the visible region were obtained with an SF-10 spectrophotometer with concentrations of 10^{-4} mole/liter.

Phenoxazin-3-one (I) was obtained according to [16], benzo[a]phenoxazin-5-one (II) was obtained according to [17], benzo[a]phenoxazin-9-one (III) was obtained according to [18], and dibenzophenoxazinones VI and VII were obtained according to [19].

LITERATURE CITED

1. L. F. Larionov, Chemotherapy of Malignant Tumors [in Russian], Moscow (1962), p. 206.
2. H. Musso and H. G. Matties, Naturwiss., 46, 15 (1959).
3. F. Kehrmann and P. Borgeaud, Helv. Chim. Acta, 9, 881 (1926).
4. K. B. Taylor, Stain Technol., 36, 73 (1961); Chem. Abs., 56, 6060.
5. G. B. Afanas'eva and I. Ya. Postovskii, Zh. Obshch. Khim., 36, 1938 (1966).
6. G. B. Afanas'eva and I. Ya. Postovskii, Khim. Geterotsikl. Soed., 5, 167 (1969).
7. J. R. Platt, J. Chem. Phys., 17, 484 (1949).
8. R. D. Brown, J. Chem. Soc., 1955 (1951).
9. G. Baldock, G. Berthier, and A. Pullman, Compt. Rend., 228, 931 (1949).
10. V. I. Minkin, A. F. Pozharskii, and Yu. A. Ostroumov, Khim. Geterotsikl. Soed., 551 (1966).
11. E. Clar, Polycyclic Hydrocarbons, 1 (1964).
12. A. Szent-Gyorgyi, Introduction to Submolecular Biology, Academic Press (1960).
13. M. A. Romanov, Collection of Programs for the "Ural" Computer [in Russian], Leningrad (1966), p. 127.
14. B. Pullman and A. Pullman, Quantum Biochemistry, Wiley (1963).
15. B. Pullman, Rev. Mod. Phys., 32, 428 (1960).
16. S. Granick, L. Michaelis, and M. P. Schubert, J. Am. Chem. Soc., 62, 1802 (1940).
17. F. Kehrmann, Ber., 28, 354 (1895).
18. O. Fischer and E. Hepp, Ber., 36, 1807 (1903).
19. H. Goldstein and H. Radovanovitch, Helv. Chim. Acta, 9, 776 (1926).