AROMATIC CYANINES

I. THEORETICAL EXAMINATION

L. S. Éfros, L. A. Ezhova,
É. R. Zakhs, and V. M. Treiger

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The cations of compounds with condensed rings containing mutually conjugated "pyridine" and "pyrrole" nitrogen atoms were considered as aromatic cyanines by the Hückel MO method. Calculation demonstrates that these sorts of cations should be thermodynamically stable and aromatic. An increase in the number of methylidyne groups between the heteroatoms leads to a bathochromic shift of the long-wave absorption band, but the magnitude of this shift also depends very much on the molecular geometry.

Cyanine dyes in which charged and uncharged heteroatoms are joined by an aliphatic chain of conjugated bonds $>\ddot{N}-(CH{=}CH)-CH{=}\overset{+}{N}<$ have one of the simplest and most effective chromophoric systems. Lengthening of the polymethine chain leads to rapid deepening of the color of these dyes with retention of a high light-absorption intensity but is accompanied by a sharp decrease in stability and lightfastness [1]. Several attempts to increase the stability of cyanine dyes by partial replacement of the aliphatic conjugated chain by aromatic groupings have been described [2, 3]. However, a more radical solution of this problem would be the synthesis of compounds in which the conjugation between the heteroatoms could be realized within a single aromatic structure. The simplest compounds of this type are apparently diazaphenalene derivatives (I-III). Only the 1,3-diazaphenalenium cation (I) has been reported [4], but it contains only one methylidyne group between the heteroatoms. The 1,4-diazaphenalenium cation (II) has three methylidyne groups, while III has five such groups.

For a further increase in the chain of conjugated bonds, it is necessary to synthesize more complex four-ring and five-ring compounds, of which the most interesting are probably IV, V, and VI. Compounds VII and VIII, which formally contain a conjugation chain of the same length, are apparently somewhat more accessible. For a preliminary estimate of the thermodynamic stability, aromaticity, and positions of the

TABLE 1. Spectral and Electronic Characteristics of Cations I-VIII

Cations	No. of methylidyne groups	Delocalization energy per electron (DE) in β_0 units)	Energy of the first electron transition (E→E*) in β_0 units	β_0, kcal/mole	Long-wave band frequency, cm^{-1}	λ_{max}, nm
I	1	0,61	−1,10	−71,5	25000	400*
II	3	0,61	−1,04	−67,5	23800	420
III	5	0,61	−1,00	−65,0	22800	440
IV	7	0,57	−0,82	−53,5	18800	530
V	9	0,54	−0,67	−43,5	16800	595
VI	9	0,54	−0,64	−41,5	14600	695
VII	7	0,57	−0,61	−39,8	14000	715
VIII	9	0,51	−0,52	−33,8	11850	845

*The experimentally found value [4, 6].

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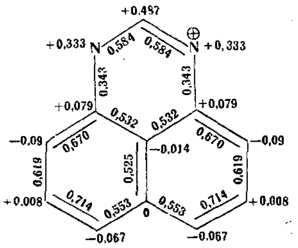
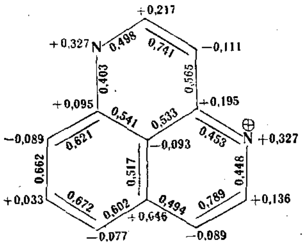
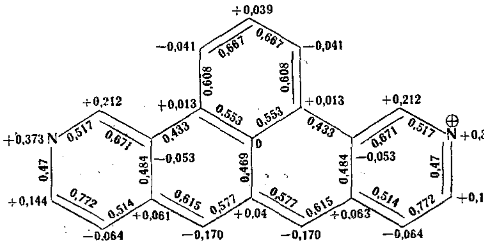
maxima of the long-wave absorption bands of I-VIII, we subjected them to quantum-mechanical calculation by the Hückel MO method (HMO).† The closed π-electron system of the perimidinium and 1,4- and 1,6-diazaphenalinium (I-III) cations consists of 14 electrons that are situated in seven bonding molecular orbitals; for all three cations, DE per electron is 0.61 β_0. In cations IV and VII, 18 π electrons occupy nine bonding orbitals in pairs, and DE is 0.57 β_0 per electron. Similarly, the 22 π electrons in V, VI, and VIII are situated in 11 bonding orbitals, and DE is 0.53 β_0. Consequently, I-VIII should be thermodynamically stable and have aromatic properties, and their aromatic stabilization decreases only slightly as the size of the molecule increases. On the basis of calculations of I-VIII, we also attempted to determine the effect of the number of methylidyne groups in the conjugated chain between the heteroatoms on the position of the maximum of the long-wave absorption band. The electronic spectrum of I has three intense absorption bands at 228, 326, and 400 nm [4, 6]. In a study of the spectra of perimidine and its derivatives, a dependence between the energies of the first electron transition (E→ E*) and the position of the long-wave absorption band was established [6]. Proceeding from the experimental $\lambda_{\max}$ of the long-wave band of I and the magnitude of E→ E* that we calculated by the HMO method, β_0 was found to be -71.5 kcal/mole. Using this β_0 value and the energies of the first electron transition of cations I-VIII, we calculated the positions of the maxima of their long-wave absorption bands (Table 1). It should be noted that the transition from I, which contains one methylidyne group, to III (five methylidyne groups) is accompanied by a bathochromic shift of the long-wave absorption band of only 40 nm. At the same time, the bathochromic shift is 90-275 nm on passing from III to compounds with seven methylidyne groups and is 155-405 nm on passing from III to compounds with nine such groups. The calculation also demonstrated that disruption of the symmetry of the cations (compare, for example, $\lambda_{\max}$ of cation VI with $\lambda_{\max}$ of V and VIII) has a pronounced effect on the energy of the first electron transition and, consequently, on the position of the long-wave band.



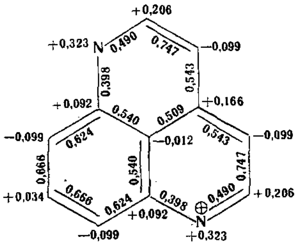
I



II



VI



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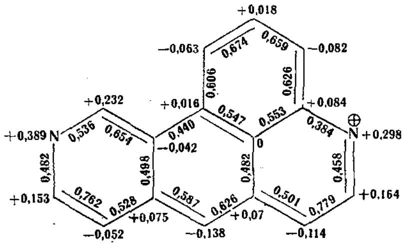
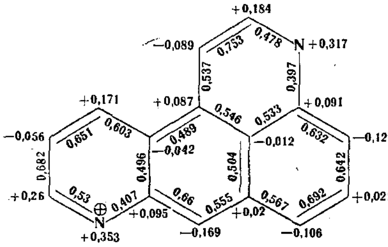
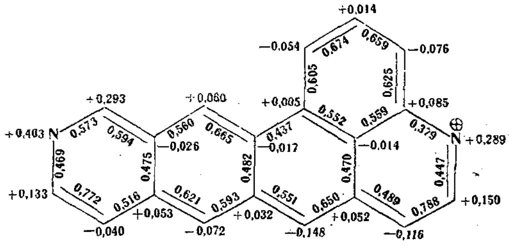


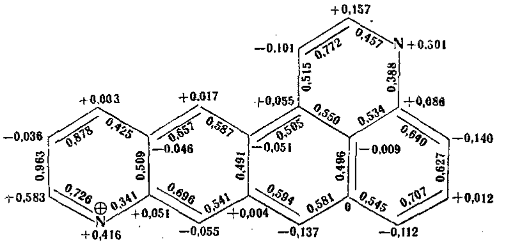
IV



VII



V



VIII

Thus an analysis of the results of the calculations makes it possible to conclude that there is a fundamental possibility for the synthesis of aromatic cyanines. An increase in the number of methylidyne groups between the heteroatoms in these compounds leads to a bathochromic shift of the long-wave absorption band, but the magnitude of the shift depends to a much greater degree on the molecular geometry.

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† Parameters representing the arithmetic means between the parameters of the two nitrogens recommended by Streitwieser [5] were taken for the heteroatoms.

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