ELECTRONIC STRUCTURE AND PHYSICAL CHEMICAL PROPERTIES OF CYCLOHEXAPYRIDINE, HEXAAZAKEKULENE, AND THEIR CLATHRATES WITH CYCLOPROPENYL CATION

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In the framework of the PPP [Pariser—Parr—Pople] method, the existence of a new class of clathrates, "aromatic in aromatic," has been shown to be possible for nitrogen-containing, aromatic macroheterocycles. Calculated values also agree well with the available experimental data for the energies of the lowest singlet-singlet and singlet-triplet transitions, the chemical shifts of protons and ^{13}C nuclei, the electric polarizability, and the diamagnetic susceptibility. An aromaticity scale is given for the systems studied.

Recently, along with known macroheterocylic systems such as the crown ethers [1], spheranes [2, p. 125], cryptanes [3], etc., the attention of investigators has been attracted to nitrogen-containing macroheterocycles [4] that appear to be a new class of ligands, promising for application in the field of selective catalysis, for the extraction of ions from solutions of low concentration, etc. Thus, following the synthesis of the hydrocarbon macrocycle kekulene containing six atoms of hydrogen in its internal cavity, cyclopyridine Ia (see Fig. 1) was prepared [5], which has a cavity of the same size and which can coordinate Na^+ as a macrocyclic ligand [6]. Hexaazakekulene, IIa, having a similar such internal cavity, was synthesized recently [7]. In this way, hydrogenated derivatives of hexaazakekulene were obtained that are capable of recovering Ca^{2+} ions from solutions of low concentration [8]. We emphasize that not only metal ions can be accommodated in the cavities of these aromatic macroheterocycles, but also the simplest of the aromatic carbocations, the cyclopropenyl cation. In compounds Ic and IIc, the distance between the proton of the cyclopropenylium ring and the nitrogen atom closest to it is 1.49 Å. This is greater than the sum of the corresponding covalent radii of hydrogen (0.28 Å) and nitrogen (0.70 Å). Thus, a question arises concerning the possible existence of a new class of clathrates, "aromatic in aromatic."

In order to explain the stability of such compounds, we have calculated the electronic structure and physical chemical characteristics of heterocycles Ia, IIa, their carbocations Ib and IIb, and the clathrates with the $C_3H_3^+$ cation, Ic and IIc in the π-electron approximation of the MO LCAO SCF method.

In the calculations, we used the density matrix formalism and the system of semiempirical parameters used earlier to describe electrical, spectral, and magnetic properties [9-12]. Here, the components of tensors of the electric dipolar polarizability and diamagnetic susceptibility and the ^1H and ^{13}C chemical shifts were obtained on the basis of a related variant of the Hartree—Fock perturbation theory. The energies of the lowest singlet-singlet transitions and the transition density matrices corresponding to them were determined as the eigenvalues and eigenvectors of the stability matrix of the Hartree-Fock ground state. The energies of the singlet-triplet transitions were determined in the Tamm-Dankov approximation.

1. We note that the inclusion of the cyclopropenylium cation in the cavity of molecules I and II reduces the symmetry of the system from D_{6h} to C_{3v}. This leads to the nonequivalence of rings 1 and 3 (of bonds 2-3 and 8-7, 3-5 and 6-7, etc., and of atoms 2 and

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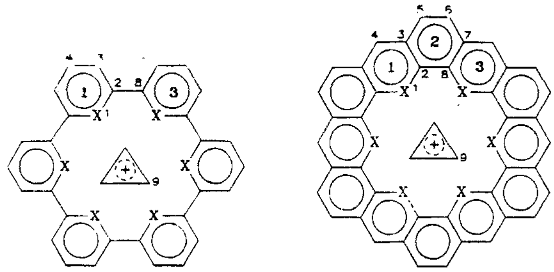

Ia-c IIa-c

Fig. 1. Ia, cyclohexapyridine (18[(2,6)pyridino$_6$crown-6]; Ib, cyclohexabenzene (18[(2,6)benzo$_6$crown-6]; Ic, the clathrate of Ia with $C_3H_3^+$; IIa, 19,20,21,22,23,24-hexaazakekulene; IIb, kekulene (cyclo[d.e.d.e.d.e.d.e.d.e.d.e.]dodecakisbenzene); IIc, the clathrate of IIa with $C_3H_3^+$. (The numbering on the figure does not correspond to IUPAC nomenclature, but was chosen for convenience of discussion; I, IIa) X = N, b) = CH; Ia, b, IIa, b) the central cation is missing.)

8, 3 and 7, 5 and 6, etc.). At the same time, calculation shows that the deviations in the charges and bond orders caused by this do not exceed 0.001-0.002 units. Consequently, the averaged values of P_{ik} as though corresponding to D_{6h} symmetry are shown in Table 1. We note also that a change in the orientation of the central ion by, let us say, its rotation about the vertex at the nitrogen atom, leads to a change in P_{ik} of the same order.

It can be seen from Table 1 that the introduction of nitrogen atoms into the carbocycles has little effect on the bond orders, and consequently, on the bond lengths. This is also true of the clathrates. In fact, the calculated values of P_{ik} agree well with the available x-ray structural data. For example, we obtained for the kekulene molecule the correlation function for bond lengths

$$l_{ik} = (1.579 \pm 0.004) - (0.299 \pm 0.007) P_{ik} \tag{1}$$

(30 points, correlation coefficient 0.983, st[andard] error 0.006 Å). This function is close to that found in [13], where, unlike our work, the resonance integral for the C—C bond is taken as 2.6 eV. The experimental deviation of molecule IIb from D_{6h} symmetry reaches 0.007 Å and is due to intermolecular interactions in the crystal. Substituting the values of the bond orders into Eq. (1), we obtain l_{2-3} = 1.394 and l_{3-4} = 1.379 Å for the C—C bonds in cyclohexapyridine. Similarly, we obtain l_{2-3} = 1.422, l_{3-4} = 1.395, l_{3-5} = 1.439, and l_{5-6} = 1.339 Å for hexaazakekulene. These values are close to the corresponding bond lengths in the clathrates and carbocyclic analogs. The 2-8 bond is the most sensitive to nitrogen substitution as well as to clathrate formation, both in the case of cyclohexabenzene and of kekulene. On nitrogen substitution, it must increase somewhat from 1.477 to 1.481 Å (in compounds Ib and Ia, respectively) and from 1.450 to 1.455 Å (in compounds IIb and IIa). The introduction of a cation into the center of the macroheterocycle will slightly increase the strength of this bond. As a consequence, there must be an insignificant shortening of the bond (to 1.480 Å in compound Ic and 1.454 Å in compound IIc).

In the calculations, compounds Ia and Ib were assumed to be planar, and no consideration was given to the possible distortion of their structures, in particular, when a cyclopropenyl cation was included in the plane of the macroheterocycles.

The residual π-electron charges varied substantially on nitrogen substitution and on the introduction of a central ion. In addition to this, attention is drawn by the almost completely identical charge distributions in compounds Ia and IIa, as well as in compounds Ic and IIc. Thus, the presence of the additional six ethylene fragments in compounds II, having no effect on the charge distributions, leads to a change in the bond orders. Comparing these distributions in the compounds studied with the residual π-electron charges of the pyridine molecule [10] (q_N = −0.177, q_2 = 0.078, q_3 = −0.006, q_4 = 0.034), we see that the pyridine fragments in these molecules preserve, by and large, the character of the electron distribution of an isolated pyridine. Binding pyridine molecules into a

TABLE 1. Residual π-Electron Charges, P_{kk}, and Bond Orders, P_{ik}

Compound	*i–k*										
	1–1	2–2	3–3	4–4	5–5	1–2	2–3	3–4	2–8	3–5	5–6
Ia	–0,157	0,071	–0,004	0,022	—	0,632	0,619	0,672	0,327	—	—
Ib	0	0	0	0	—	0,633	0,622	0,670	0,341	—	—
Ic	–0,242	0,070	0,020	0,061	—	0,620	0,622	0,668	0,331	—	—
IIa	–0,157	0,069	0,0	0,034	–0,007	0,625	0,527	0,618	0,414	0,469	0,804
IIb	0	0	0	0	0	0,624	0,530	0,616	0,430	0,470	0,803
IIc	–0,243	0,064	0,008	0,077	0,010	0,612	0,530	0,615	0,419	0,471	0,803

closed sextet leads, basically, to a decrease (according to the model) in the charge of the nitrogen atom; i.e., to a reduction of its basicity. The further introduction of a cation into the center of the molecule leads to the polarization of the π-electron cloud and the draining of the negative charge on the nitrogen atoms. We note that, in contrast to the case of pyridine, where the bond orders are equalized almost as in benzene, one finds a less equable distribution of bond orders in compounds Ia, IIa, and also in Ic and IIc. In accordance with Klar's rule of sextets [15], the bond orders in type 1 rings of set II compounds should have an equalized character: the 3-5 and 2-8 bonds should be weakened and the 5-6 bond should be essentially double. According to Table 1, the calculation is in complete accord with this rule. From this point of view, the molecules of set II compounds consist of "perturbed" molecules of set I compounds. Clearly, this circumstance is explained by the similarity of the charge distributions in compounds Ia and IIa and in Ic and IIc. In connection with this, it is of interest to consider the distribution of directed ring currents in these compounds in order to explain the agreement of Klar's rule of sextets with the aromaticity, characterizable by π-electron ring currents.

2. Attention is drawn to the absence of currents flowing around the macrocycle ($\dot{I}_{2-8} = 0$) in the compounds of set I. In these compounds, the currents are completely localized in the pyridine (Ia, Ic) or benzene (Ib) rings and somewhat less than the current in isolated pyridine or benzene rings. At the same time, as in the case of benzene, nitrogen substitution in cyclohexabenzene increases the directed current somewhat. The presence of a cation in the center of the macrocycle lowers its value. Overall, the aromaticity of set I compounds determined by the ratio of diamagnetic susceptibilities, $\chi' = \chi^{\pi}/\chi_{\text{benzene}}$, proves to be less than the aromaticity of six benzene or pyridine rings.

In set II compounds, the choice of contours about which the π-electron ring currents flow (see, for example, [17]) is ambiguous. Thus, the current distributions shown in Table 2 should be treated as a diamagnetic current ($\dot{I}_{5-6}$) flowing around the exterior perimeter of the molecule, a paramagnetic current ($\dot{I}_{2-8}$) flowing around the interior contour, and a diamagnetic current flowing around the pyridine rings ($\dot{I}_1 = \dot{I}_{1-2} - \dot{I}_{2-8} = \dot{I}_{3-4} - \dot{I}_{5-6}$). It can be seen from Table 2 that nitrogen substitution leads to a drop in the current in both the exterior and interior rings and to an increase in the currents in the pyridine fragments. The introduction, however, of a central ion in compound IIa decreases the currents in the exterior contour and the pyridine rings and increases the current around the interior perimeter of the macroheterocycle.

A different choice of nonconducting contours of the molecule is also possible. In particular, it is possible to choose contours for set II compounds such that the currents flowing around them will be only diamagnetic. Then, the current distributions shown in Table 2 can be pictured as diamagnetic currents flowing around the pyridine ring ($\dot{I}_1 = \dot{I}_{1-2}$), around the benzene ring ($\dot{I}_2 = \dot{I}_{2-8}$), and around the external perimeter of the molecule ($\dot{I} = \dot{I}_{3-4} - \dot{I}_{1-2} = \dot{I}_{5-6} - \dot{I}_{2-8}$). The results of the calculation show that nitrogen substitution leads to an increase in the current in the pyridine ring and a decrease in $\dot{I}_2$ and $\dot{I}_1$, and that the introduction of a central ion leads to an increase in $\dot{I}_1$ and $\dot{I}_2$ and to a sharp drop, practically to zero, in the current around the exterior perimeter.

It follows from the calculated data that pyridine ring (1) is more aromatic than ring 2; i.e., $\dot{I}_1 > \dot{I}_2$. This agrees with Klar's rule of sextets, according to which the aromaticity of ring 2 is less than that of ring 1 in view of the substantial double bond nature of the 5-6 bond. As a whole, the diamagnetic susceptibility of molecules of set II compounds characterized by χ', is essentially higher than the diamagnetic susceptibilities at

TABLE 2. The Physical Chemical Molecular Characteristics of the Macroheterocycles

Compound	Directed π-electron ring currents*				Diamagnetic susceptibilities		Electric polarizabilities × 10^{25} cm^3		Conjugation energy, kcal/mole	Energy of lowest transition, eV	
	$\dot{i}_{1-2}$	$\dot{i}_{3-4}$	$\dot{i}_{2-8}$	$\dot{i}_{5-6}$	χ'	$\chi_m \cdot 10^6$, cm^3/mole	$\alpha_{xx}^{\pi}=\alpha_{yy}^{\pi}$	$\bar{\alpha}$		λ_1^s	λ_1^T
Ia	0,921	0,921	0	—	5,52	253	672	582	2159	3,96	2,81
Ib	0,909	0,909	0	—	5,46	295	638	611	2150	3,86	2,80
Ic	0,909	0,909	0	—	5,51	275	706	627	2302	3,89	2,85
IIa	1,235	1,328	0,846	0,938	14,25	409	1186	893	2949	2,91	1,98
IIb	1,224	1,326	0,850	0,952	14,38	453	1194	940	2941	2,86	1,96
IIc	1,269	1,281	0,907	0,920	13,55	421	1195	927	3094	2,80	2,06

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*Directed, π-electron ring currents were calculated by the method in [16].

the 12 (six, for molecules of I) isolated benzene rings. This is in contrast to molecules of set I compounds. Here, the nitrogen substitution lowers χ' slightly and then, with the introduction of a central ion, substantially reduces the aromaticity (χ') of the hexaazakekulene. We note that the current in the ring of the $C_3H_3^+$ cation does not depend on the environment and equals the current of the isolated, cyclopropenyl cation, $\dot{I} = 0.333$, $\chi' = 0.056$.

From the data in Table 2, it is possible to construct a scale of aromaticity of the systems investigated, arranging them in order of increasing χ'. Comparing the relative diamagnetic susceptibilities of compounds Ia-c, IIa-c, and compounds of other classes, it is possible to construct a general aromaticity scale. Thus, comparing the data in Table 2 with the results of calculations of χ' of porphyrins [17], we see that set II compounds are more aromatic than chlorine, azaporphines, porphine, and monobenzoporphines and less aromatic than metalloporphine and phthalocyanine.

On the basis of a calculation of the π-electronic contributions to the diamagnetic susceptibilities, and using an additive scheme to take account of the σ-skeleton [10, 18], we calculated the molar, diamagnetic susceptibilities, χ_m, experimental values of which have been hitherto lacking (Table 2).

We note that, unlike cyclopolyenes and porphyrins, where the contributions of the current to the chemical shifts of exterior and interior protons have different signs, these values in compounds Ib and IIb have the same sign because of the current distributions described above, and strong screening of the interior protons should not be observed.

3. It is not difficult to calculate the chemical shifts of the protons and ^{13}C nuclei by the method in [10, 16-18] on the basis of the charge and current distributions in the molecules investigated (see Table 3). We note that, overall, the calculation does not agree badly with the available experimental data. Thus, the measured protonic chemical shifts for the kekulene molecule (δ: 8.01 (5-H), 8.45 (4-H), and 10.44 (1-H) ppm [19]) correspond somewhat better to those we have calculated than to those obtained by a modified Hückel method [20] (8.01 (5-H), 8.78 (4-H), and 8.67 (1-H)) or by the MacWhinney method of ring currents [19] (7.70 (5-H), 8.25 (4-H), and 10.26 (1-H)). We note that our calculated protonic chemical shifts for kekulene virtually coincide with those obtained by Vogler [21], which were also obtained in the framework of a related variant of Hartree-Fock perturbation theory (8.22 (5-H), 8.71 (4-H), 10.42 (1-H)).

Comparing the calculated chemical shifts of compounds IIb and Ib, we see that the introduction of six ethylene fragments into a molecule of Ib leads to a shift of the signals from both interior and exterior protons to weaker fields by about 1.5 ppm. It can also be seen from Table 3 that the effect of nitrogen substitution (in both compounds Ib and IIb) on the protonic chemical shifts is weakly expressed, in contrast to the effect on the chemical shifts of the ^{13}C nuclei. This is explained by the similarity of the current distributions in compounds Ia and Ib (IIa and IIb) and the strong dependence of the local contributions to the chemical shifts of ^{13}C nuclei on the residual π-electron charges on the nuclei being screened. The results of a calculation of the magnetic screening of the ^{1}H and

TABLE 3. Chemical Shifts of ^{1}H and ^{13}C Nuclei (δ, ppm relative to TMS)

Compound	Nucleus							
	1-H	3-H	4-H	5-H	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$
Ia	—	7,96	7,19	—	157,9	126,6	130,1	—
Ib	8,96	7,91	7,13	—	136,2	127,0	126,8	—
Ic	—	8,51	7,71	—	158,6	130,7	136,4	—
IIa	—	—	8,80	8,18	154,2	132,2	132,4	127,6
IIb	10,44	—	8,76	8,20	132,7	132,2	127,4	128,5
IIc	—	—	9,22	8,57	154,4	134,1	139,5	130,5

^{13}C nuclei in a cyclohexapyridine molecule (hexaazakekulene is yet to be synthesized) agree overall with the experimental data from [5] (8.13 (5-H), 7.81 (4-H), 156.6 ($C_{(2)}$), 122.0 ($C_{(13)}$), and 137.8 ($C_{(4)}$)). The deviations from the experimental values can be ascribed to the nonplanar structure of compound Ia although it was assumed to be planar in the calculation. The available experimental values of the protonic chemical shifts for dodecahydro-IIa, whose π-electronic skeleton coincides with that for the Ia molecule, but is planar, amount to 7.60 (4-H), which agrees better with the calculation even without allowing for the effect of the ethane fragments.

The introduction of a central ion leads to a weak (~0.4-0.5 ppm) shift of all the proton signals to weaker fields, whereas the relative change in the chemical shifts of the ^{13}C nuclei is smaller. The chemical shifts of the nuclei in the cyclopropenyl cation are not considered in the present work because of the presence of hydrogen bonds to the macroheterocycles (an allowance for which has not been developed in the framework of the procedure used). In addition, the chemical shifts of the protons of the macrocycle, calculated for the Ic clathrate, are close to the experimental values for the complex of Na^{+} with symmetrical, diphenyl-substituted cyclohexapyridine [6]: 7.4, 7.8, and 8.6 (H) ppm (cf. with data in Table 3).

4. The energies of the lowest electronic transitions, assigned to symmetries of $^{1}E_{2g}$- and $^{3}B_{1u}+$ (see Table 2), were calculated. For the compounds investigated, nitrogen substitution leads to a weak hypsochromic shift of the bands of these symmetries. When a cyclopropenyl cation is introduced into the cavity, a bathochromic shift of the fluorescence band of the macroheterocycle is observed. The bands corresponding to the lowest triplet transition undergo a further hypsochromic shift. In the case of kekulene, IIb, the wavelength of the transition, λ_1 = 2.55 eV, corresponds, not to $^{1}E_{2g}$-symmetry as in the other compounds investigated, but to $^{1}B_{2g}$-symmetry (the transition of $^{1}E_{2g}$-symmetry is also given in the Table). Another two singlet transitions were calculated for the kekulene molecule, ($^{1}B_{1u}+$) 3.13 and ($^{1}E_{2g}+$) 3.37 eV, which correspond to experimental data [14]: phosphorescence, 2.08-2.12 eV; fluorescence, 2.74 eV, and absorption, 3.23, 3.50, 3.76 eV.

Considering the electronic structure of the excited state presented in Table 2, one can state the following: excitation of the molecule leads to an increase in the negative charge on the nitrogen atoms in singlet states and to a decrease in this charge in triplet states. When a central ion is introduced, these changes are increased. Excitation of the molecules leads to a loosening of the bonds, and only the 2-8, 3-5, and 6-7 bonds in set II compounds are strengthened insignificantly. Calculation showed that according to the criteria in [22], the transitions considered are delocalized over the entire molecule.

The contribution from π-electrons to the components of the electric polarizability tensor and its average value α, (see [23]) were calculated. The σ-skeletons were taken into account with the help of an additive scheme. The presence of unshared pairs of the nitrogen atoms, the differing electrical properties of the C—C and C—N bonds, etc., were allowed for by means of a single empirical constant that equalled -2.147×10^{-25} cm^3.

The conjugation energy of the investigated compounds was calculated by the method in [24] (Table 2). It can be seen that nitrogen substitution lowers the energy of the molecule, and that the introduction of a central ion leads to an analogous result. Using the energies of conjugation of clathrates Ic and IIc and of macroheterocycles Ia and IIa, and allowing for the fact that the conjugation energy of $C_3H_3^{+}$ amounts to 114.7 kcal/mole, it is easy to obtain the energy of "confinement" of the cyclopropenyl cation. For cyclohexapyridine, it comes to 28.8 kcal/mole, and 30.1 kcal/mole for hexaazakekulene (independent of the orientation of the ion in the cavity of the ring). This exceeds the energy of an N—N single bond, for example. The lower limit of the equilibrium constant corresponding to these values is ~10^{22}.

Thus, a calculation by the PPP method shows that the purely electrostatic interaction of $C_3H_3^+$ with the polarized macroheterocycle (even without taking account of hydrogen bonding) is able to confine the molecular ion within the interior cavity of the ligand. In other words, an "aromatic in aromatic" class of clathrates based on nitrogen-containing macroheterocycles is capable of existence.

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