REACTIONS OF CYCLAMMONIUM CATIONS

XXVIII.* 4,9-DIAZAPYRENE IN HETARYLATION REACTIONS

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UDC 547.834:541.67:543.422.25.4.6

The π-electron charges, bond orders, energies of the singlet and triplet electronic transitions, and the PMR spectrum of 4,9-diazapyrene were calculated by the self-consistent-field (SCF) method with allowance for the coulombic repulsion, and the results are compared with the experimentally found positions of the long-wave bands in the UV spectrum and the experimental PMR spectrum. 4,9-Diazapyrene hetarylates activated aromatic and heteroaromatic rings.

Until recently there was no theory that enabled one to predict the behavior of any of the nitrogeneous heteroaromatic systems in hetarylation reactions of organic compounds in the presence of acylating agents. The first step in this reaction is the formation of aromatic N-acylcyclammonium salts [2]. A necessary, but not always sufficient, condition for the participation of the heterocycle in the hetarylation reaction is therefore the presence in it of a pyridine nitrogen atom that is capable of interacting with the acyl halides. Of no less importance is the magnitude of the electrophilicity of the resulting hetarylating agents, which, all other conditions being equal, depends on the magnitude of the effective positive charge on the α (or γ-)-carbon atom of the ring of the starting molecule of the heterocycle and the polarizability of the N=C bonds in the course of the reaction during the formation of N-acylheteroaromatic cations. It was recently shown that an exocyclic CH=N group is more predisposed to such reactions than a ring CH=N group [3]. Aromatic Schiff bases in the presence of acyl halides prove to be convenient α-amidomethylating agents for many nucleophilic organic compounds [3]. In this connection, it was expedient to examine the behavior in this reaction of 4,9-diazapyrene, in which the tendency for an increase in the order of the ring nitrogen–carbon bond is clearly expressed. To estimate the reactivity of 4,9-diazapyrene, we calculated the bond orders and distribution of the π-electron density; the coulombic repulsion between the electrons was taken into account in order to obtain the most reliable data.

We also used the previously developed method of direct calculation of the charge-bond order matrix [4] without prior distribution of the orbital coefficients, which makes it possible to achieve self-consistency with a high degree of accuracy. The program in [5] which makes it possible to directly obtain analogous values that characterize the transition from the ground state to the excited state was used in the calculation of the excited states. This method is equivalent to a considerable extent to the Pariser–Parr method for excited states, but with the conditon that the set of excited configurations used is a standard set that includes all of the singly excited configurations, regardless of the size of the system. This insures identical physical conditions for the introduction of the parameters and makes the calculation more reliable. We selected the parameters that characterize the carbon atom from the spectra of a large group of hydrocarbon molecules [5, 6]: the resonance integral $\beta_{CC} = -2.45$ eV and the function that characterizes the coulombic repulsion is

$$\gamma(R) = \frac{10.1397}{\sqrt{a^2+R^2}} + \frac{0.1460}{\sqrt{0.05^2+R^2}}\ (\text{eV}), \tag{1}$$

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*See [1] for communication XXVII.

Donetsk State University. Donetsk Physical-Organic Chemistry Branch, Institute of Physical Chemistry, Academy of Sciences of the Ukrainian SSR. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 537-541, April, 1974. Original article submitted May 25, 1973.

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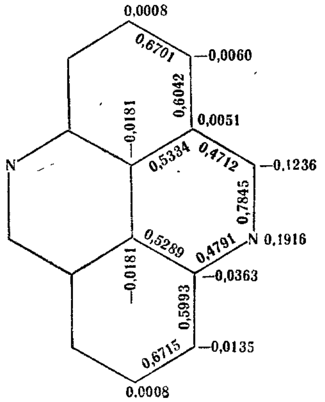
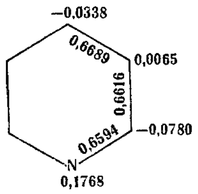
where $a_C = 2.2$ and R is in "bond length" units of 1.4 Å.

Parametrization of the nitrogen atom, the difference of which from the carbon atom was as usual, characterized by its electronegativity $\delta\omega_N = -1.68$ eV, by $\beta_{CN} = -2.57$ eV, and the shielding coefficient $a_N = 1.3558$ for the determination of γ_{NN} from expression (1), was in addition necessary for the calculation of diazapyrene. The $\gamma_{CN}(R)$ value when $a_{CN} = (a_N + a_C)/2 = 1.7779$ is similarly obtained. These parameters were also selected from the electronic spectra of a series of nitrogen heterocycles of the 1,4-bis(2-vinylpyridyl)benzene and benzoquinoline types.





In order to verify the electron distribution of 4,9-diazapyrene, which is represented by the molecular diagram above, we simultaneously calculated its electronic spectrum and compared it with the experimental spectrum. The electronic spectrum of pyridine was also calculated for comparison (Table 1). In the known calculations of the spectra of polycyclic nitrogen-containing heterocycles [7], the electronic interaction is taken into account with respect to perturbation theory with the superimposition of two to four configurations. As it turned out, our method of computation [4] is applicable to a more extensive number of investigated objects and is more systematic in a theoretical respect. As seen from Table 1, not only are the three lower absorption bands in the pyridine molecule, the assignment of which corresponds to the data in other studies [10, 11], in satisfactory agreement with the experiments [8, 9], but the lower triplet level is also in good agreement with the fluorescence maximum [9]. Two close and quite intense bands of the same symmetry, which can be compared with the α and p bands of pyrene, which are also close to one another (3.24 and 3.50 eV) are observed in the spectrum of 4,9-diazapyrene.

The PMR spectra of 4,9-diazapyrene and pyridine which are in good agreement with the experimental spectra (Table 2) were also calculated by the method adopted for hydrocarbons [13], but with additive addition to the nitrogen atom.

TABLE 1. Energies of the Electron Transitions (eV)

Compound	Symmetry	Singlet			Triplet	
		calc.	f	exptl.	calc.	exptl.
Pyridine	A	6,30 7,47	0,01 0,91	6,36[8] 7,04	3,78 4,49	3,69[9, 10]
	B	4,65 8,05	0,03 0,12	4,96 —	4,26 5,24	
4,9-Diazapyrene	B	3,21 3,36	0,291 0,214	3,3—3,5[12]	1,19 3,35	
	A	4,20 5,88	— —	4,07 5,24	3,20 4,23	
Pyrene	B_{3u}^- (α) B_{2u}^+ (p)	3,24 3,50	— 0,542	3,3—3,5 3,5—3,6	— 1,94	— 2,08

TABLE 2. PMR Spectra

Hydrogen atom	Pyridine, δ, ppm		4,9-Diazapyrene, δ, ppm	
	calc.	exptl. data [14]	exptl. data	calc.
2-H	8,44	8,29	8,23	8,18
3-H	7,05	6,77	9,13	9,49
4-H	7,09	7,15	—	—
5-H	—	—	8,55	8,59

TABLE 3. Acyl Derivatives of Tetrahydrodiazapyrene (II-IV)

Compound	React. conditions		.mp, °C	R_f	Empirical formula	Found				Calc.				Yield, %
	temp., °C	time, h				C, %	H, %	N, %	Mol. wt.	C, %	H, %	N, %	Mol. wt.	
IIa	80	3	229—230[a]	0,24	$C_{44}H_{30}N_4O_2$	80,5	5,3	8,7	625	81,7	4,7	8,7	646	60
IIb	30—50	2	180—181[b]	0,14	$C_{34}H_{26}N_4O_2$	76,3	5,3	11,1	536	78,2	5,0	10,7	523	50
IIc	100—110	10—12	160—161[c]	0,75	$C_{46}H_{34}N_4O_2$	80,5	5,9	7,6	670	81,8	5,1	8,3	675	43
IId	100—110	10—12	175—176[d]	0,17	$C_{46}H_{34}N_4O_2$	79,1	5,3	8,6	671	81,8	5,1	8,3	675	45
IIe	110—120	10	153—154[e]	0,66	$C_{44}H_{38}N_4O_2$	79,3	5,8	9,2	625	80,7	5,8	8.5	655	51
IIf	100	11	155—156[f]	0,58	$C_{38}H_{30}N_4O_2$	78,2	5,5	7,7	587	79,5	5,2	9,7	576	50
IIg	110—120	10—12	145—146[e]	0,18	$C_{48}H_{34}N_4O_2$	80,7	5,1	7,8	701	82,5	4,9	8,0	698	40
III	100	10	216—217[f]	0,27	$C_{26}H_{18}N_2O_2$	78,2	5,8	8,3	378	80,0	4,6	7,2	390	35
IV	110	14	221—222[f]	0,40	$C_{28}H_{20}N_2O_2$	80,4	4,8	8,3	430	80,7	4,6	6,7	416	50

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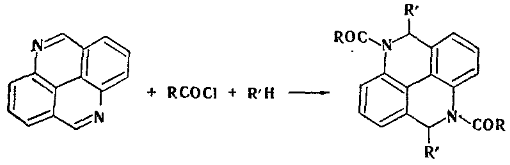
[a] From petroleum ether–pentanol. [b] From pentanol. From aqueous methanol. [d] From chloroform. [e] From ether–petroleum ether. [f] From aqueous acetone.

The results of the calculation of the spectra of 4,9-diazapyrene and pyridine satisfactorily reproduce the entire experimental picture, and for this reason the calculated distribution of the electron density of these molecules presented in the diagrams may provide the basis for a discussion of their chemical properties.

In addition to this, the basicity of 4,9-diazapyrene, which proved to be somewhat lower than the pK_a value of pyridine and approximately equal to the basicity of aniline, determined in a similar manner [16] (10.40, 12.33, and 10.56, respectively), was also measured by the method in [15].

Thus, the set of calculated and experimental data, which confirm the high C–N bond order, the relatively high basicity, and the considerable deficit of π-electron charge on the α-carbon atom, made it possible to assume that 4,9-diazapyrene has high activity in hetarylation reactions.

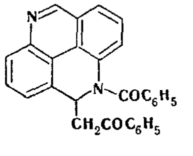
In fact, the corresponding 5,10-disubstituted 4,9-diacyl-4,5,9,10-tetrahydro-4,9-diazapyrenes (Table 3) were obtained at room temperature or on brief heating of a mixture of 4,9-diazapyrene and acyl halides with nucleophilic aromatic and heteroaromatic compounds.



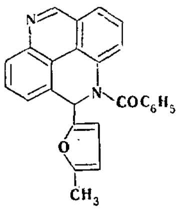
II

a $R=C_6H_5$, $R'=$3-indolyl; (b) $R=CH_3$, $R'=$3-indolyl; (c) $R=C_6H_5$, $R'=$1-methyl-3-indolyl (d) $R=C_6H_5$, $R'=$2-methyl-3-indolyl (e) $R=C_6H_5$, $R'=C_6H_4N(CH_3)_2$-p; (f) $R=C_6H_5$, R' = 1-methyl-2-pyrrolyl (g) $R = C_6H_5$, R' = 1-phenyl-2-pyrrolyl

Heteroaromatic systems containing two nitrogen atoms of the pyridine type usually form monosubstituted compounds (for example, m-phenanthroline and phthalazine in reactions with benzoyl chloride and KCN [17]) in such reactions. For the first time we have apparently been able to obtain disubstituted II, but monosubstituted compounds, for example, III and IV, are also formed in some cases:

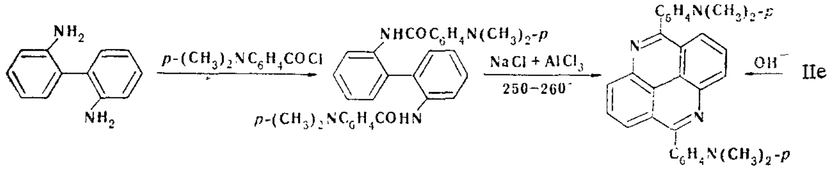


III



IV

There are characteristic bands of ν_{CO} stretching vibrations at 1670-1700 cm^{-1} in the IR spectra of I-IV. In contrast to II, III and IV form picrates; this confirms their structures. The structure of one of the compounds (IIe) was proved by alternative synthesis via the scheme



V VI

The IR and UV spectra of IIa-g are similar to the spectra of IIe; this confirms the structure assigned to them.

EXPERIMENTAL

The IR spectra of chloroform solutions were recorded with a UR-10 spectrometer. The PMR spectrum of a dimethyl sulfoxide solution was recorded with a YaMR-5535 spectrometer (40 MHz) with cyclohexane as the internal standard. Chromatography in a loose thin layer of Al_2O_3 was accomplished with benzene–hexane–chloroform (6 : 1 : 30).

4,9-Diazapyrene was obtained by fusing 2,2'-diformamidodiphenyl with NaCl and $AlCl_3$ at 250°. The product had mp 218-220° (from ethanol) (mp 220-221° [12]).

Typical method of hetarylation. A solution of 0.005 mole of thoroughly dried 4,9-diazapyrene, 0.01 mole of acyl chloride, and 0.01 mole of the compound to be hetarylated in 25 ml of anhydrous benzene was held at 25° or 100° for 2 to 12 h, depending on the nucleophilicity of the compound to be hetarylated (see Table 3), after which the solution was made alkaline with ammonia and steam distilled. The residue in the flask was separated, washed with water, dried, and recrystallized from suitable solvents. The yields and characteristics of the compounds obtained are presented in Table 3.

5,10-Di(p-dimethylaminophenyl)-4,9-diazapyrene (VI). **A.** A solution of 2.5 g (45 mmole) of KOH in 20 ml of 70% ethanol was added to 0.5 g (0.8 mmole) of IIe, and the mixture was refluxed for 20 h. It was then cooled, and the precipitate was removed by filtration and recrystallized from alcohol to give 0.18 g (40%) of a product with mp 277-278° and R_f 0.83. Found: C 80.8; H 7.4; N 12.1%. $C_{30}H_{28}N_4$. Calculated: C 81.1; H 6.3; N 12.6%.

B. A mixture of 1.9 g (0.01 mole) of 2,2'-diaminodiphenyl, 4.6 g (0.025 mole) of p-dimethylaminobenzoyl chloride, and 2 g of potassium carbonate in 20 ml of ether was refluxed for 3 h, after which it was diluted with water. The resulting precipitate was separated, washed with water, dried, and recrystallized from ethanol to give 2.4 g (50%) of 2,2'-bis(p-dimethylaminobenzamido)diphenyl (V) with mp 166-167° and R_f 0.35. Found: C 74.4; H 6.6; N 12.0%. $C_{30}H_{30}N_4O_2$. Calculated: C 73.8; H 6.1; N 11.4%.

A 0.82-g (0.05 mole) sample of V was added in portions to a melt consisting of 3.7 g of NaCl and 17.7 g of $AlCl_3$ at 150°, after which the temperature was raised to 250-260° and maintained there for 8 h. The mixture was then poured over ice, and the aqueous mixture was made alkaline and extracted with benzene. The extract was dried, the benzene was removed by distillation, and the residue was separated with a column filled with Al_2O_3 with elution with benzene–hexane–chloroform (6 : 1 : 30) to give 0.1 g of diazapyrene VI with mp 272-274°, which proved to be identical to the sample described above.

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