SPIROYPYRANS FROM NITROGEN HETEROCYCLES

APPLICATION OF THE MO METHOD

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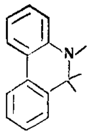
Calculation by the LCAO MO method showed that the formation and stability of spiropyrans obtained by the condensation of quaternary salts of nitrogen heterocycles with salicylaldehyde depend on the magnitude of the positive charge on the carbon atom at which the pyran ring is closed and on the magnitude of the localization energy of this reaction center. New representatives of spiropyrans based on 5,10-dimethyl-4,9-diazapyrene were synthesized.

Deeply colored merocyanines, which are incapable of intramolecular cyclization to form spiropyran derivatives [1, 2], are formed by the reaction of salicylaldehyde with 1,2-dimethylpyridinium (I) and 1,2-dimethylquinolinium (II) cations. On the other hand, the corresponding products from 5,6-dimethylphenanthradinium (III) and 9,10-dimethylacridinium (IV) cations are colorless spiropyrans [2,3]. To establish the reasons upon which the possibility of the formation of spiropyrans depend, we used the LCAO MO method in the Hückel approximation to calculate the molecular diagrams of the ground states of I-IV and, as a unique standard, that of the 1,1,2-trimethyl-3H-indolinium cation (V), since V is widely used in the synthesis of spiropyrans [4]. The same calculation of the appropriate dihydro derivatives of the A type, which are models of the nitrogen-containing portion of spiropyrans from I-V, was carried out simultaneously to compute the localization energy.



A

The h_X, k_{CX}, and δ values taken from [5] were used in the calculation. The inductive effect from only the quaternized nitrogen atom was taken into account. The methyl group was considered to be a pseudoheteroatom contributing a 2π electron to the overall π system: h_{CH_3} 4 and k_{C-CH_3} 0.45 [6]. The localization energy was calculated as the difference between the π-electron energies of the dihydro derivative and the

TABLE 1. Reactivity Indexes and Structures of the Condensation

Cation	$+q$	p	$-L$	Condensation product
I	0,1813	1,5298	11,3120	Merocyanine
II	0,2418	1,5389	11,1566	Merocyanine
III	0,3277	1,5788	10,9194	Spiropyran
IV	0,3128	—	11,1088	Spiropyran
V	0,5788	1,7114	11,0644	Spiropyran
VI	0,3312	1,5789	10,7596	Spiropyran
VII	0,3321	1,5819	10,9576*	Spiropyran

*Since there are no reaction centers in dication VII, the value 0.5L is presented.

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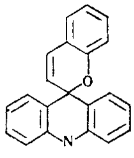
cation. The results are presented in Table 1, where q is the resulting charge on the carbon atom at which the pyran ring is closed, p is the bond order between this atom and the nitrogen atom, and L is the localization energy in units of β_0.

The data obtained indicate that the formation of closed or open forms in the condensation of quaternary salts with salicylaldehyde is determined by the q and p values. In fact, I and II have the minimum q values, and the products of the reaction of these substances with salicylaldehyde have merocyanine structures. The q value is larger in the remaining compounds, and the condensation of III-V with salicylaldehyde results in the formation of spiropyrans. The same dependence in the case of α-methyl derivatives is observed from a comparison of the p values. The results of the calculation are in agreement with the proposal of a relationship between the electrophilicity of a reaction center and the possibility of the formation of spiropyrans in reactions of this type [2, 3]. It is apparent that the change in the localization energies (L) is not symbatic with respect to the sequence of the change in q and p. A comparison of the data presented in Table 1 makes it possible to relate the L values to the capacity of spiropyrans for ring opening. Thus the largest L values correspond to substances obtained from I and II and are merocyanines. The spiropyran from V is capable of ring opening on irradiation with UV light or on heating [3, 4]. The L value of this spiropyran is lower than the L value of the spiropyrans from I and II, which do not actually exist. The spiropyran from III has an even lower L value, which is in accordance with the preliminary data on the high stability of the spiropyran ring of this substance as compared with the spiropyran obtained on the basis of V. The noncorrespondence between the L value of the acridine spiropyran (VIII), which is close to the L value of the spiropyran from V, and the fact that VIII does not display thermochromic properties and is much less photochromic than the spiropyran obtained on the basis of V [7] seems somewhat surprising. It seems to us that in this case one should take into account the structural factors which distinguish VIII from the other spiropyrans of the investigated series. Hydrogen atoms in the 4- and 5-positions can hinder opening of the ring of VIII and the appearance of a coplanar conjugated system.



VIII

Thus the results make it possible to assume that the L value characterizes the capacity of spiropyrans for reversible ring opening. We note that if the use of L for comparison with the thermochromic properties is valid, it is apparently impossible to arrive at a judgment regarding the possibility of the manifestation of photochromic properties from the magnitude of this index alone. Photochromic transformations are complex and are determined not only by thermodynamic relationships [7, 8].

It was of interest to verify the applicability of the above conclusions to similar 4,9-diazapyrene derivatives [9]. As we already reported in [10], a peculiarity of diazapyrene is its tendency for reactions with nucleophilic reagents, as a consequence of which one might have expected increased activity of the methyl groups in 5,10-dimethyl-4,9-diazapyrene (IX) and especially in its mono- and diquaternary salts (VI and VII). As a test for the lability of the hydrogen atom, we selected the condensation of VI and VII with salicylaldehyde.* On the one hand, the products of this reaction are of interest as potential photo- and thermochromic substances while, on the other hand, they are of interest as new objects for the verification of the above conclusions. Compound VI was obtained in almost quantitative yield by treatment of IX with methyl iodide under pressure and also by heating IX in chlorobenzene with dimethyl sulfate. The appearance of a strong electron-acceptor center sharply inhibits the alkylation of the second nitrogen atom, and VII is not formed under these conditions. Compound VII could be synthesized by the action of methyl p-toluenesulfonate on IX. The use of this alkylating agent made it possible to dispense with the hard-to-obtain and inconvenient-to-use triethyloxonium borofluoride, used in the synthesis of the diquaternary salts of the isomeric (to IX) 2,7-diazapyrene [11]. As seen from Table 1, the annelated pyridine ring in VI and VII barely changes its q, p, and L values as compared with III. It should have been expected that the products of the reaction of VI and VII with salicylaldehyde could exist as spiropyrans and have properties close to those of the spiropyrans from III. In fact, almost colorless spiropyrans (X and XI) were isolated by the

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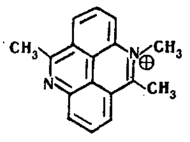
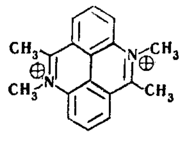
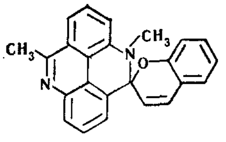
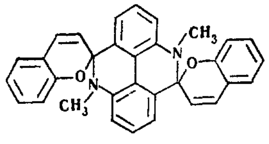
*R. P. Polyakova participated in the experimental work.

condensation of VI and VII with salicylaldehyde under conditions which were identical to those used to obtain a spiropyran from III [2]. Preliminary tests indicate the similarity between the photo- and thermochromic properties of X and XI and those of the spiropyran based on III. Compound XI is apparently as yet the only known representative of spiropyrans which contain two spiro atoms in one heterocycle.


VI


VII


X


XI

EXPERIMENTAL

4,5,10-Trimethyl-4-azonium-9-azapyrene Iodide (Iodide of VI). A mixture of 1.2 g of 5,10-dimethyl-4,9-diazapyrene (IX) and 33 ml of methyl iodide was heated in a sealed tube at 130° for 5.5 h. After cooling, 1.9 g (98%) of the iodide of VI was filtered. This was crystallized twice from water (1 : 10), washed with the minimum amount of alcohol and ether, and vacuum dried to give orange crystals with mp 217-219° (decomp.), which are crystallized from alcohol, soluble in acetone and chloroform, and insoluble in ether. R_f 0.3 * (chloroform, violet fluorescence in UV light which vanishes after several minutes, and a dark spot appears). Found %: I 32.3; N 7.7. $C_{17}H_{15}IN_2$. Calculated %: I 33.9; N 7.5. The borofluoride of CI was obtained by the addition of $NaBF_4$ to an aqueous solution of the iodide of VI and was crystallized from water to give green crystals with mp 228-234° (decomp.), UV spectrum (water), λ_{max}, nm (log ε): 238 (4.60), 270 (3.97) shoulder; 278 (4.01); 340 (3.68) shoulder; 350 (3.73), 373 (3.69); 391 (3.82). The UV spectrum in alcohol was not subject to the dilution law. PMR spectrum† : 0.6 ppm ($C-CH_3$, 6H); 1.8 ppm ($N-CH_3$, 3H). Found %: N 8.4. $C_{17}H_{15}BF_4N_2$. Calculated %: N 8.4. The methylsulfate of VI was obtained from 0.5 g (2 mmole) of IX and 0.3 ml (3 mmole) of dimethyl sulfate by refluxing in 20 ml of chlorobenzene for 4 h, cooling, and filtering to give 0.74 g (96%) of green crystals with mp 230-235° (decomp.). The compound was crystallized from propanol (1 : 500). Found %: C 60.0; H 5.4. $C_{18}H_{18}N_2O_4S$. Calculated %: C 60.3; H 5.0.

4,10-Dimethylspiro[4,5-dihydro-4,9-diazapyrene-5,2'-[2H-1]benzopyran] (X). The iodide of VI [0.15 g (0.4 mmole)] was dissolved by boiling in 50 ml of alcohol, 0.04 ml (0.4 mmole) of salicylaldehyde, and 0.25 ml (2.5 mmole) of piperidine were added, and the solution was refluxed for 1 h. The mixture was then cooled, 100 ml of water was added, and 0.1 g (72%) of X was filtered. It was reprecipitated from alcohol with water using activated charcoal and crystallized from cyclohexane to give almost colorless crystals with mp 191-193° which were soluble in carbon tetrachloride and chloroform. R_f 0.6 (chloroform, dark blue fluorescence in UV light which disappears after several minutes, and a dark spot appears). UV spectrum (alcohol), λ_{max}, nm (log ε): 218 (4.59); 225 (4.54) shoulder; 254 (4.35); 277 (4.01) shoulder; 377 (3.57). Found %: C 82.0; H 5.5. $C_{24}H_{18}N_2O$. Calculated %: C 82.2; H 5.2.

4,5,9,10-Tetramethyl-4,9-diazoniumpyrene Ditosylate (Ditosylate of VII). A mixture of 1.1 g of IX and 9 g of methyl p-toluenesulfonate was heated at 180° for 1.5 h, suspended in a small volume of ethanol, and 2.68 g (94%) of a dark-gray substance was filtered. A total of 1 g of the product was dissolved by boiling in 540 ml of ethanol and 20 ml of water, the solution was cooled, and 130 ml of butanol was added. Lustrous silvery plates (0.4 g) with mp 310-312° (decomp.) began to precipitate in a short time. The ditosylate of VII was crystallized from water (1 : 3), was soluble in dimethylformamide, and insoluble in ether. R_f 0.2 [chloroform–acetone (7 : 3), rose fluorescence in UV light which changes to an intensely black spot after 5-10 min]. Found %: C 63.8; H 5.5; N 4.8. $C_{32}H_{32}N_2O_6S_2$. Calculated %: C 63.5; H 5.3; N 4.7. The diborofluoride of VII was obtained and crystallized in the same way used for the borofluoride of VI and was

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*Activity II Al_2O_3 was used in all cases for the thin-layer chromatography.

† The chemical shifts of the protons at weaker field relative to the signal of $(CH_3)_4NCl$ as the internal standard in concentrated H_2SO_4 are presented here.

obtained as silvery, light-brown plates with mp 340-341° (decomp.). The PMR spectrum was similar to the PMR spectrum of the borofluoride of VI, and the ratio of the integral intensities of the N−CH_3 and C−CH_3 signals was 1:1. UV spectrum (water), λ_{max}, nm (log ε): 215 (4.43); 235 (4.49) shoulder; 242 (4.61); 260 (4.20); 270 (4.21); 328 (3.92); 343 (4.00); 372 (3.77); 392 (4.06); 470 (2.43). UV spectrum (88% alcohol), λ_{max}, nm (log ε): 225 (4.55); 257 (4.21); 322 (3.90); 480 (3.32). Found %: N 6.4. $C_{18}H_{18}B_2F_8N_2$. Calculated %: N 6.5.

4,9-Dimethyldispiro[4,5,9,10-tetrahydro-4,9-diazapyrene-5,10,2',2"-bis[2H-1]benzopyran] (XI). A total of 0.5 g (0.8 mmole) of the ditosylate of VII was dissolved by boiling in 350 ml of alcohol, 0.18 mole (1.7 mmole) of salicylaldehyde and 1 ml (10 mmole) of piperidine were added, and the mixture was refluxed for 10 min. It was then cooled, 120 ml of water was added, and 0.27 g (69%) of XI was filtered. It was crystallized twice from chlorobenzene−alcohol (2:3) to give slightly yellowish crystals with mp 269-270° which were soluble in chlorobenzene (1:100) and dimethylformamide, slightly soluble in benzene, and insoluble in alcohol. UV spectrum (benzene), λ_{max}, nm (log ε): 274 (4.56); 308 (4.31); 365 (4.27). Found %: C 82.4; H 5.3; N 5.9. $C_{32}H_{24}N_2O_2$. Calculated %: C 82.0; H 5.2; N 6.0.

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