INVESTIGATIONS IN THE FIELD OF SYNTHETIC DYES

LXXI. Condensation of N-Aryllepidinium Salts with Sodium Anti-p-nitrobenzenediazotate*

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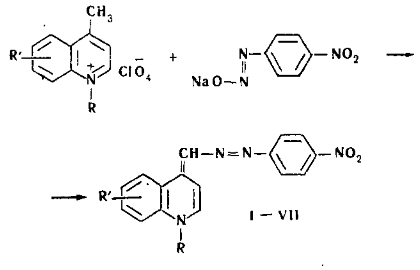
The interaction of sodium anti-p-nitrobenzenediazotate with a number of N-aryllepidinium salts yields previously unreported ethyleneazo dyes the solvatochromic properties of which have been studied. By the action of acids, these substances are converted into arylhydrazones.

The reaction of quaternary salts of heterocyclic bases with sodium anti-p-nitrobenzenediazotate [1] is the most convenient method of obtaining ethyleneazo dyes with a nitro group in the para position [2–4].

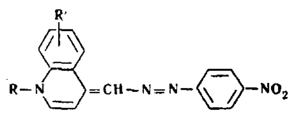
In the present paper we give the results of a study of the reaction of sodium anti-p-nitrobenzenediazotate with a number of N-aryllepidinium salts [5–8]: N-phenyl-, 6-methyl-N-(p-tolyl)-, 6-methoxy-N-(p-methoxyphenyl)-, 6-bromo-N-(p-bromophenyl)-, N-phenyl-5,6-benzo-, and N-(β-naphthyl)-5,6-benzolepidinium perchlorates. For comparison, N-methyllepidinium perchlorate was also used in this reaction.

We have found that the above-mentioned quaternary salts readily condense with sodium anti-p-nitrobenzenediazotate on heating in ethanolic solution in the following way.

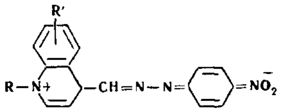


The ethyleneazo compounds (I–VII) isolated (Table 1) form deep blue-black pulverulent substances readily soluble in pyridine and acetone, sparingly in ethanol and ether, and insoluble in water. They dissolve in organic solvents with a deep blue coloration and have a single absorption band in the 590–625 nm region.

The actual structure of the molecule of an ethyleneazo dye is intermediate between the two extreme structures **A** and **B**. In the unexcited state, structure A predominates, and in the excited state the energetically less favorable bipolar structure **B**



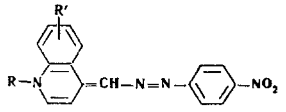
A



B

The decrease in the basicity of the quinoline nucleus with the addition of electrophilic substituents to the nitrogen heteroatom and in position 6 must raise the energy of the excited state (structure IB), which leads to a hypsochromic shift of the absorption maximum. In actual fact, the replacement of an alkyl radical by an electron-accepting phenyl radical on the nitrogen heteroatom (I and II) leads to a hypsochromic shift of the absorption maximum by 6 nm. The introduction of two bromine atoms (V) causes the same effect to an even greater extent. Conversely, electron-donating substituents (CH_3, OCH_3, the 5,6-benzo group), by increasing the basicity of the quinoline nucleus, lower the energy of excitation of structure IB. This leads towards an equalization of the energy of the two structures, which causes a shift of the absorption maximum in the direction of

Table 1



Compound	R	R'	Mp, °C (decomp.)	λ_{max}, nm (ethanol)	log ε	Empirical formula	N, % found	N, % calculated	Yield, %
I	CH_3	H	207—208	614	4,33	$C_{17}H_{14}N_4O_2$	18.56; 18.72	18.29	71
II	C_6H_5	H	176—177	608	4,63	$C_{22}H_{16}N_4O_2$**	15.34; 15.42	15.21	84.5
III	p-$CH_3C_6H_4$	6-CH_3	208—210	622	4,65	$C_{24}H_{20}N_4O_2$	14.17; 14.23	14.13	79.5
IV	p-$CH_3OC_6H_4$	6-OCH_3	156—157*	628	4,61	$C_{24}H_{20}N_4O_4$	12.88; 13.02	13.08	75.5
V	p-BrC_6H_4	6-Br	225—226*	600	4,53	$C_{22}H_{14}Br_2N_4O_2$	10.82; 10.76	10.65	81.5
VI	C_6H_5	5,6-Benzo	178—179	623	4,52	$C_{26}H_{18}N_4O_2$	13.89; 13.92	13.39	96.5
VII	β-$C_{10}H_7$	5,6-Benzo	222—223	590	4,50	$C_{30}H_{20}N_4O_2$	12.02; 12.24	11.96	95

*Without a solvent.

**Found, %: C 71.52; 71.47; H 4.61; 4.69. Calculated, %: C 71.73; H 4.38.

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*For part LXX, see [8].

Table 2

Absorption Maxima of the Ethyleneazo Dyes Derived from Quaternary Salts of Lepidine in Various Solvents

Compound	Dioxane	Benzene	Acetone	Methanol	Nitrobenzene	Dimethylformamide	Formamide*
I	590	590	602	608	626	626	640
II	578	582	600	606	616	616	634
III	590	591	616	617	636	636	644
IV	600	600	628	628	652	652	654
V	566	575	593	600	618	618	—
VI	590	595	617	622	638	638	652
VII	570	570	590	590	610	610	618

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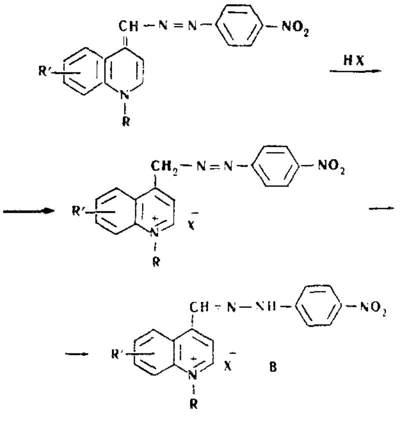
*With the addition of alkali.

greater wavelengths. We see this on passing from compound II to III, IV, and VI. From a comparison of compounds VI and VII, it can be seen that the electron-accepting nature of a β-naphthyl radical on the nitrogen heteroatom is expressed considerably more strongly than that of a phenyl radical in the same position, which leads to a considerable hypsochromic effect.

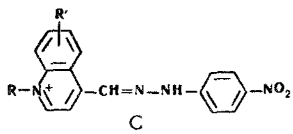
Ethyleneazo compounds are known to have the property of changing their color in various neutral solvents (solvatochromy) [2]. We have studied this property in more detail for our compounds and have found that these compounds possess positive solvatochromy (Table 2). By its polarizing action, the solvent lowers the energy of excitation of structure B, which causes the energies of the two structures to become closer and the absorption maximum to shift bathochromically with an increase in the polarity of the solvent.

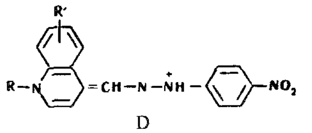
On adding a molecule of acid, ethyleneazo compounds give salt-forming substances having the structure of hydrazones (Table 3). This process is accompanied by a heightening of the color to yellow-orange. Salt formation evidently takes place in two stages.



The treatment of a solution of an arylhydrazone with alkali leads to the re-formation of compounds I-VII.

The actual structure of the hydrazone is intermediate between the two limiting structures C and D.


C


D

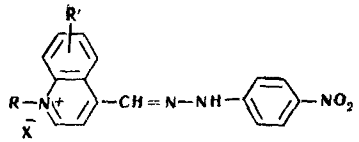
In the unexcited state, structure C predominates, and in the excited state the energetically less favorable structure D, since the basicity of the nitrogen of an imino group is much less than that of the nitrogen heteroatom of the quinoline nucleus because of the influence of the electrophilic nitro group in the para position. The relatively highly excited state causes a high coloration of compounds VIII-XVI. The decrease in the basicity of the quinoline nucleus due to the presence of electrophilic substituents on the nitrogen heteroatom and also in position 6 leads to a lowering of the energy of excitation of state D with the result that the absorption maximum shifts into the long-wave part of the spectrum. We observed this by comparing the absorption maxima of compounds VIII with IX, IX with XIV, and VIII with XV. Nucleophilic substituents act in the opposite direction and therefore heighten the color of the arylhydrazone (compare IX with XII, XIII and XV).

EXPERIMENTAL

N-Methyllepidinium perchlorate. A four-necked flask fitted with a mechanical stirrer, reflux condenser, and two graduated burettes was charged with 27 ml (0.3 mole) of hydrochloric acid (d 1.19), 75 ml of acetone, and 25 ml of nitrobenzene. A solution of 22 ml (0.2 mole) of N-methylaniline in 68 ml of acetone was placed in one burette, and 50 ml (0.25 mole) of formaldehyde solution and 40 ml of water in the second. The contents of the flask were heated to the boil with vigorous stirring in the water bath and uniformly, every 3 min, 2 ml of the N-methylaniline solution and 2 ml of the formaldehyde solution were added alternately to the flask from the burettes. After the addition of the solutions, the reaction mixture was boiled with stirring for another 10 hr. At the end of the reaction, the acetone and the nitrobenzene were distilled off. The solution was filtered, evaporated, and treated with 57 ml (0.2 mole) of 30% $HClO_4$, whereupon the quaternary salt precipitated in the form of an oil which solidified on cooling. After crystallization from water it formed yellowish needles with mp 153° C [9]. Yield 17.5 g (34%). Found, %: C 50.94; 51.4; H 4.82; 5.01; Cl 13.53; 13.59; N 5.40; 5.22. Calculated for $C_{11}H_{12}ClNO_4$, %: C 51.2; H 4.67; Cl 13.7; N 15.18.

4-Nitrophenylazomethylene-1-phenyl-1,4-dihydroquinoline (II). A mixture of 1 g (3.1 mM) of N-phenyllepidinium perchlorate, 0.59 g (3.1 mM) of sodium anti-p-nitrobenzenediazotate, and 10 ml of ethanol was heated at a gentle boil for 10 min. The crystals were filtered off and the residue on the filter was washed with hot water. After reprecipitation with water from pyridine, the dye was recrystallized from ethanol. This gave a deep blue-black microcrystalline powder with mp 176°-177° C. Yield 1.07 g. The dye gave a red-orange halochromic compound with concentrated H_2SO_4. It is readily soluble in acetone, sparingly in ethanol, and insoluble in water.

Table 3



Compound	R	R′	X	Mp, °C (decomp.)	λ_{max}, nm (ethanol)	log ε	Empirical formula	Element	Found, %	Calculated, %	Yield, %
VIII	CH_3	H	ClO_4	281—282	474	4.63	$C_{17}H_{15}ClN_4O_6$	N Cl	13.88; 13.92 8.69; 8.61	13.70 8.73	49
IX	C_6H_5	H	Cl	276—277	485	—	$C_{22}H_{17}ClN_4O_2$	N Cl	13.87; 13.97 8.85; 8.92	13.84 8.77	29
X			HSO_4	282—283	486	—	$C_{22}H_{18}N_4O_6S$	N	12.26; 12.08	12.02	48
XI			ClO_4	264—265	485	4.60	$C_{22}H_{17}ClN_4O_6$	N Cl	11.73; 11.82 7.73; 7.71	11.86 7.58	59
XII	p-$CH_3C_6H_4$	6-CH_3	ClO_4	267—268	481	4.59	$C_{24}H_{21}ClN_4O_6$	N Cl	11.34; 11.42 6.98; 7.05	11.20 7.15	61.4
XIII	p-$CH_3OC_6H_4$	6-OCH_3	ClO_4	240—241*	483	4.57	$C_{24}H_{21}ClN_4O_8$	N Cl	10.67; 10.72 6.87; 6.91	10.50 6.71	49
XIV	p-BrC_6H_4	6-Br	ClO_4	259—260	493	4.57	$C_{22}H_{15}Br_2ClN_4O_6$	N Br+Cl	9.07; 9.17 31.5; 31.3	8.93 31.20	69
XV	C_6H_5	5.6-Benzo	Cl	232—233	478	4.48	$C_{26}H_{19}ClN_4O_2$	N Cl	12.57; 12.61 8.03; 8.13	12.30 7.81	47
XVI	β-$C_{10}H_7$	5.6-Benzo	ClO_4	279—280	470	4.51	$C_{30}H_{21}ClN_4O_6$	N Cl	10.05; 10.17 6.21; 6.18	9.85 6.24	64

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*Without decomposition

Found, %: C 71.88; 71.96; H 4.76; 5.05; N 15.06; 15.02. Calculated for $C_{22}H_{16}N_4O_2$, %: C 71.55; H 4.60; N 15.18.

Compounds I and III-VII were obtained similarly.

p-Nitrophenylhydrazone of 4-formyl-1-phenylquinolinium perchlorate (XI). With heating, 0.2 g (0.54 mM) of compound II was dissolved in 25 ml of acetone and the solution was treated with an excess of $HClO_4$ and poured into a large volume of hot water. After cooling, the orange precipitate was filtered off. Crystallization from a mixture of acetone and ethanol (1:1) gave XI in the form of lustrous purple-red crystals.

Compounds VIII-XVI were obtained similarly.

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