LITERATURE CITED

1. B. Holmberg, Ark. Kemi, 2, 567 (1950); Chem. Abstr., 46, 100 (1952).
2. F. Bohlmann and E. Bresinsky, Chem. Ber., 97, 2109 (1964).
3. V. N. Elokhina, A. S. Nakhmanovich, I. D. Kalikhman, N. P. Sokol'nikova, and M. G. Voronkov, Khim. Geterotsikl. Soedin., No. 10, 1328 (1975).
4. V. N. Elokhina, R. V. Karnaukhova, A. S. Nakhmanovich, I. D. Kalikhman, and M. G. Voronkov, Zh. Org. Khim., 15, 57 (1979).
5. K. Hideg, O. Hideg-Hankovszky, and P. Sohar, Chem. Ber., 107, 2079 (1974).
6. M. I. Rybinskaya, Zh. Vses. Khim. Ova., 12, 12 (1967).
7. S. I. Miller, C. E. Orzech, C. A. Welch, G. R. Zeigler, and J. I. Dichstein, J. Am. Chem. Soc., 84, 2020 (1962).

ELECTRONIC STRUCTURES AND REACTIVITIES OF POLYMETHINE DYES AND THEIR DERIVATIVES

P. I. Abramenko and A. N. Gusarov

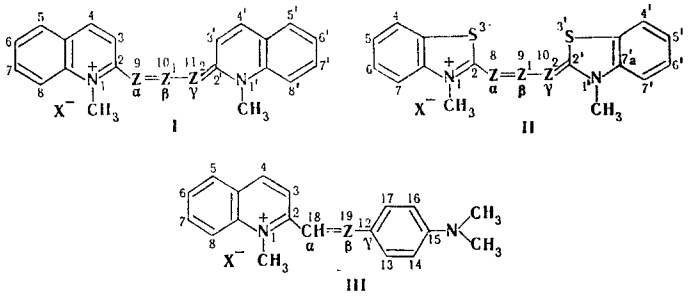
UDC 547.789.61'831:668.819.45:540.14.5

The peculiarities of the electronic structures of polymethine dyes that contain one or two nitrogen atoms in the chromophore were examined by means of the self-consistent-field (SCF) method within the Pariser–Parr–Pople (PPP) approximation as compared with the electronic structures of the corresponding trimethylidynecyanines, viz., benzothiazole and 2-quinoline derivatives, which are spectral sensitizers of silver halide emulsions.

It is known that some 2-quino- and thiacarbocyanines, as well as p-dialkylaminostyryl dyes that contain nitrogen atoms in the external polymethine chain, have a pronounced desensitizing effect when they are introduced into silver halide photographic emulsions [1]. The desensitizing abilities of such compounds depend on the location of the nitrogen atom in the chain [2, 3].

It seemed of interest to investigate the peculiarities of the electronic structures and reactivities of such dyes as compared with the corresponding sensitizing thia- and 2-quinocyanines that do not contain a nitrogen atom in the chromophore.

In the present communication we discuss the results of quantum-chemical calculations of the electronic structures of dyes I–III:



Z, Z¹ and (or) Z²=CH or N

The calculations were made by the molecular orbital self-consistent-field (MO SCF) method within the Pariser–Parr–Pople (PPP) approximation by means of the program in [4] and the parameters and computational procedure described in [5, 6]. In the calculations all of the angles were assumed to be 120°, except for the following angles in dyes II: 108°C (in the thiazole rings of the heteroresidues) and 126° (the 3–2–8, CH_3–1–2, 1–2'–1', and CH_3–1'–7'a angles). All of the bonds were assumed to be 1.397 Å, except for the following bonds in the chromophore (in angstroms): C–C (1.360), N–CH_3 (1.470), C=C (1.460), N=C (1.420), N–C (1.310), and N=N (1.390).

All-Union State Scientific-Research and Design Institute of the Photographic Chemical Industry, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1492–1494, November, 1982. Original article submitted December 30, 1981.

 0009-3122/82/1811-1156$07.50

TABLE 1. Charges on the Atoms (q_r) and Bond Orders (p_{rs}) of Dyes I-III in the Ground Singlet State ($^1S_0$)

Compound	In I-III			q_r							p_{rs}					
	Z	Z'	Z''	N_1	C_2	C_α (N_α)	C_β (N_β)	C_γ (N_γ)	$C_{2'}$	$N_{1'}$	N_1—C_2	C_2—C_α (C_2—N_α)	C_α—C_β (N_α—N_β)	C_β—C_γ (N_β—N_γ)	C_γ—$C_{2'}$ (N_γ—$C_{2'}$)	$C_{2'}$—$N_{1'}$
A	—	N	—	0,293	0,206	−0,383	—	—	0,209	0,290	0,476	0,576	—	—	0,577	0,475
B	—	CH	—	0,277	0,128	−0,169	—	—	0,128	0,277	0,442	0,616	—	—	0,616	0,442
Ia	CH	CH	CH	0,293	0,100	−0,121	0,124	−0,121	0,124	0,293	0,438	0,607	0,639	0,607	0,639	0,438
Ib	CH	N	CH	0,281	0,115	−0,034	−0,122	−0,034	0,115	0,281	0,439	0,578	0,655	0,655	0,578	0,439
I'b	N	N	CH	0,283	0,188	−0,288	−0,044	−0,015	0,146	0,301	0,456	0,608	0,560	0,739	0,509	0,469
Ic	N	CH	CH	0,289	0,200	−0,345	0,214	−0,131	0,137	0,280	0,469	0,587	0,598	0,660	0,603	0,447
Id	N	CH	N	0,295	0,213	−0,349	0,301	−0,348	0,214	0,293	0,479	0,568	0,624	0,623	0,570	0,477
IIa	CH	CH	CH	0,382	0,124	−0,122	0,151	−0,122	0,124	0,382	0,576	0,648	0,630	0,630	0,648	0,576
IIb	N	N	CH	0,274	0,219	−0,278	−0,027	−0,050	0,187	0,305	0,497	0,621	0,577	0,727	0,530	0,530
IIc	N	CH	CH	0,278	0,236	−0,341	0,230	−0,166	0,173	0,272	0,510	0,603	0,605	0,650	0,622	0,492
IId	N	CH	N	0,285	0,254	−0,345	0,312	−0,376	0,251	0,276	0,524	0,576	0,640	0,603	0,588	0,526
IIIa	CH	—	—	0,303	0,151	−0,096	0,165	−0,067	0,091	0,154	0,474	0,513	0,760	0,460	0,569*	0,402
IIIb	N	—	—	0,314	0,146	0,033	−0,097	−0,013	0,092	0,158	0,481	0,448	0,785	0,482	0,552*	0,405

*For the C_γ—$C_{1'}$ bond.

TABLE 2. Charges on the Atoms (q_r) and Bond Orders (p_{rs}) of Dyes I-III in the Excited Singlet State ($^1S_1$)

Compound	q_r							p_{rs}					
	N_1	C_2	α	β	γ	$C_{2'}$	$N_{1'}$	N_1—C_2	C_2—α	α—β	β—γ	γ—$C_{2'}$	$C_{2'}$—$N_{1'}$
A	0,257	0,017	−0,161	—	—	0,020	0,255	0,366	0,576	—	—	0,576	0,366
B	0,249	−0,061	0,104	—	—	0,061	0,249	0,347	0,564	—	—	0,564	0,347
Ia	0,276	−0,026	0,096	−0,044	0,096	−0,026	0,276	0,373	0,551	0,617	0,617	0,551	0,373
Ib	0,257	−0,022	0,158	−0,259	0,158	−0,022	0,257	0,370	0,558	0,611	0,611	0,558	0,370
I'b	0,277	0,086	−0,077	−0,189	0,165	−0,046	0,252	0,406	0,602	0,568	0,643	0,527	0,360
Ic	0,268	0,063	−0,176	0,036	0,109	−0,029	0,257	0,398	0,577	0,618	0,587	0,562	0,365
Id	0,268	0,055	−0,157	0,119	−0,154	0,056	0,266	0,391	0,571	0,606	0,605	0,572	0,390
IIa	0,400	−0,073	0,049	−0,096	0,049	−0,073	0,400	0,491	0,620	0,594	0,594	0,620	0,491
IIb	0,292	0,072	−0,102	−0,246	0,093	−0,065	0,279	0,439	0,637	0,544	0,610	0,583	0,412
IIc	0,279	0,044	−0,190	−0,030	0,055	−0,054	0,276	0,433	0,607	0,598	0,564	0,602	0,405
IId	0,281	0,035	−0,183	0,036	−0,217	0,038	0,276	0,424	0,604	0,585	0,574	0,607	0,421
IIIa	0,239	−0,078	0,081	−0,041	0,096	0,135	0,241	0,342	0,528	0,664	0,499	0,506*	0,471
IIIb	0,239	−0,084	0,158	−0,251	0,171	0,148	0,258	0,342	0,506	0,683	0,491	0,489*	0,486

*For the C_γ—$C_{1'}$ bond.

The charges (q_r) and bond orders (p_{rs}) in the ground ($^1S_0$) and excited ($^1S_1$) singlet states, as well as the reactivity indexes, were calculated. The interaction of 14 excited configurations was taken into account in the calculations.

It follows from Table 1 that dye Ib, which is a desensitizer, differs from spectral sensitizer Ia with respect to the presence of significant negative charge on the meso atom of the external polymethine chain (N_β). A smaller degree of negative charge of the meso atom of the external chain than in the case of Ib is characteristic for dye I'b, which is a desensitizer and a weak sensitizer. It should be noted that in desensitizing dyes Ib and I'b the negative charge is localized on all of the atoms of the external polymethine chain. Dye Ic, which has a sensitizing effect, is similar to sensitizer Ia with respect to the character of the electron-density distribution in the polymethine chromophore. Although to a smaller degree, the same is also characteristic for dye Id, which is known to be a weak sensitizer.

With respect to the character of the electron-density distribution in the polymethine chromophore, dyes with the II structure with benzothiazole residues are similar to the corresponding 2-quinoline derivatives: IIa is a sensitizer, II'b is a desensitizer and a weak sensitizer, IIc is a sensitizer, and IId is a weak sensitizer.

The same principles are also peculiar to dyes with the III structure. Thus the presence of a negative charge on all of the atoms of the external polymethine chain is characteristic for the dyes that have a desensitizing effect. The higher the magnitude of the negative charge on its meso atom, the more markedly expressed the desensitizing effect of the dye. Higher magnitudes of the charges on the α, β, and γ atoms of the external chain than

TABLE 3. Reactivity Indexes of the Atoms of the Chromophors of Dyes I-III with Respect to Electrophilic (p_E) and Nucleophilic (p_N) Reagents

Compound	p_E							p^*_N						
	N_1	C_2	C_α	C_β	C_γ	$C_{2'}$	$N_{1'}$	N_1	C_2	C_α	C_β	C_γ	$C_{2'}$	$N_{1'}$
A	0,061	0,001	0,414	—	—	0,001	0,061	0,124	0,352	0,000	—	—	0,357	0,125
B	0,090	0,019	0,547	—	—	0,019	0,090	0,126	0,367	0,000	—	—	0,367	0,126
Ia	—	—	0,401	—	0,401	—	—	—	0,427	—	—	—	0,427	—
Ib	0,085	0,053	0,452	0,000	0,451	0,053	0,084	0,115	0,316	0,027	0,277	0,026	0,324	0,118
Ib	0,085	0,010	0,477	0,015	0,391	0,021	0,055	0,065	0,169	0,037	0,296	0,013	0,436	0,162
Ic	0,061	0,011	0,348	0,032	0,511	0,022	0,083	0,094	0,268	0,006	0,354	0,001	0,351	0,120
Id	0,056	0,001	0,377	0,000	0,377	0,001	0,056	0,105	0,297	0,002	0,337	0,001	0,309	0,108
IIa	—	0,037	0,380	0,000	0,380	0,037	—	—	0,433	0,011	0,520	0,011	0,433	—
IIb	0,135	0,003	0,343	0,005	0,290	0,013	0,071	0,071	0,244	0,060	0,457	0,048	0,593	0,155
IIc	0,094	0,004	0,257	0,015	0,362	0,001	0,104	0,085	0,358	0,021	0,562	0,008	0,518	0,116
IId	0,085	0,003	0,214	0,001	0,202	0,001	0,068	0,094	0,408	0,019	0,582	0,008	0,460	0,100
IIIa			0,261		0,346	0,200	0,354	0,175	0,470		0,380			
IIIb			0,250		0,369	0,215	0,348	0,186	0,476		0,288			

*The p_N values for C_4 of the pyridine ring in III (Z = CH) and III (Z = N) are 0.392 and 0.393, respectively.

for the corresponding dyes that have higher photographic efficiency are characteristics for the compounds with a weak sensitizing effect.

In the excited singlet state (Table 2) the charges on the carbon atoms of the chromophore in dyes I-III are reversed. The negative charge of the N atom is retained in this case. The electron density of the chromophore in aza derivatives of dyes I-III is generally delocalized to a smaller extent than in quino-2,2'- and thiacyanines, and this is responsible for the differences in their colors.

The data in Table 3 show that the introduction of nitrogen atoms into the polymethine chain of dyes I-III [Z, Z^1 and (or) Z^2 = N] also leads to substantial changes in the reactivities of the C atoms of the chromophore with respect to electrophilic and nucleophilic reagents.

It should be noted that the calculated lowest vacant levels of the desensitizing dyes with I-III structures, in which the methylidyne group in the polymethine chromophore is replaced by a nitrogen atom, are 0.4-0.6 eV lower than the levels of the corresponding spectral sensitizers.

LITERATURE CITED

1. C. Mees and T. James, Theory of the Photographic Process, Macmillan (1966).
2. J. D. Kendall, British Patent No. 447109; Chem. Abstr., 30, 6666 (1936).
3. L. G. S. Brooker, L. F. White, and R. H. Spraque, J. Am. Chem. Soc., 73, 1087 (1951).
4. V. A. Kosobutskii, Master's Dissertation, Rostov-on-Don (1974).
5. P. I. Abramenko and V. A. Kosobutskii, Khim. Geterotsikl. Soedin., No. 5, 626 (1978).
6. P. I. Abramenko, A. N. Gusarov, and V. A. Kosobutskii, Zh. Prikl. Spektrosk., 31, 91 (1979).