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QUANTUM-CHEMICAL CALCULATIONS OF THE ELECTRONIC STRUCTURES OF POLYMETHYLIDYNE DYES

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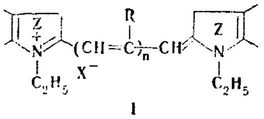
UDC 547.749'829:541.67:668.819.45

The energies of the transitions of unsubstituted and substituted thia-, thiazolo-, and thienothiazolocarbocyanines, as well as quinocyanines and carbocyanines with a condensed thiophene, furan, selenophene, or pyridine ring, to the excited singlet states and their electronic structures were calculated by the MO LCAO method within the Pariser—Parr—Pople approximation. The nature of the long-wave and short-wave absorption bands in the spectra of these dyes and the peculiarities of the color of thieno-, furo-, and selenophenothiazolo- and -pyridocyanines, as well as the effect of substituents on their electronic characteristics as a function of the position in the heteroresidues and the nature of the latter, are discussed.

Polymethylidyne dyes are of interest as spectral sensitizers of motion picture photographic materials. Information regarding their electronic structures is extremely valuable for the interpretation and prediction of their various properties.



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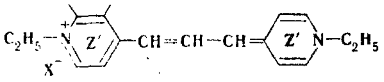


II

In the present research we investigated the electronic structures and colors of a number of cyanine dyes with structures I and II, in which Z is unsubstituted or substituted thiazolyl, benzothiazolyl, furo- and thieno[3,2-d]thiazolyl, benzoxazolyl, 3,3-dimethylindoleninyl, 1-ethylbenzimidazolyl, 2-pyridyl, 2-quinolyl, thieno-, selenopheno-, or furo-[2,3-b]-6-pyridyl, Z' is 4-pyridyl, 4-quinolyl, 5-vinyl-4-pyridyl, thieno-, furo-, or selenopheno[2,3-b]-4-pyridyl, n = 0–3, R = H, CN, or $N(C_2H_5)_2$, and X^- is an acid residue.

The calculations were made by the Pariser—Parr—Pople method with the program described in [1]. The $\gamma_{\mu\nu}$ integrals were calculated from the Mataga—Nishimoto formula [2]. The $\beta_{\mu\nu}$ resonance integrals were calculated with the "variable β" approximation [3, 4]. The principal parameters and the details of the calculation were presented in [5]. The parameters for nitrogen in the heteroresidues were determined from the tables of Hinze and Jaffe [6] by the Pariser—Parr procedure [7]. The constants for variation of $\beta_{\mu\nu}$ for the C-S bond and the W_μ and $\gamma_{\mu\mu}$ values for the sulfur atom were borrowed from [8]. At the beginning of the calculation, all of the rings were considered to be regular polygons with bond lengths of 1.40 Å. The C-C and C=C bond lengths were assumed to be 1.48 and 1.36 Å, respectively, and the valence angles were assumed to be 120°. However, during the calculation the geometrical characteristics were recalculated in conformity with the procedure proposed in [9]. The parameters for the N and O atoms in the NO_2 and OCH_3 groups, the C and N atoms in the CN

All-Union Scientific-Research Institute of Synthetic Resins, Vladimir 600006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 626-633, May, 1978. Original article submitted September 7, 1977.

0009-3122/78/1405-0511$07.50

TABLE 1. Energy and Spectral Characteristics of Dyes with the I Structure

Z in formula I with R = H	$-E_{tot}$, eV	$E^{th}_{0\to 1}$		$f_{0\to 1}$	$E^{exp}_{0\to 1}$		$E^{th}_{0\to 2}$		$f_{0\to 2}$
		eV	nm		eV	nm	eV	nm	
2-Pyridyl	231,183	2,255	549	1,497	2,200	560	3,370	368	0,008
5-Vinyl-2-pyridyl	280,946	2,105	589	1,765	—	—	3,187	389	0,025
2-Quinolyl	332,440	2,032	610	1,906	2,043	607	3,429	381	0,007
Selenopheno[2,3-b]-6-pyridyl	—	1,982	625	—	—	—	—	—	—
Thieno[2,3-b]-6-pyridyl	352,544	2,023	613	1,409	2,006	618	3,444	318	0,143
Furo[2,3-b]-6-pyridyl	364,397	2,015	615	1,367	2,00	620	3,466	327	0,245
Thiazolyl	241,698	2,313	536	1,142	2,284	543	4,065	305	0,102
5-Vinylthiazolyl	291,572	2,124	584	1,290	—	—	4,00	311	0,184
4-Phenylthiazolyl	398,899	2,238	554	1,306	2,214	560	—	—	—
4-Styrylthiazolyl	449,372	1,187	567	1,263	2,168	572	—	—	—
5-Aminothiazolyl	318,169	2,145	578	1,347	2,137	580	—	—	—
5-Nitrothiazolyl	380,662	1,933	633	1,178	1,943	638	—	—	—
5-Phenylthiazolyl	399,048	2,087	594	1,229	2,094	592	—	—	—
5-Styrylthiazolyl	444,632	1,933	641	1,392	1,956	634	3,370	368	0,410
Thieno[2,3-d]thiazolyl	354,563	2,130	582	1,413	2,087	594	3,523	317	0,110
Benzoxazolyl	374,851	2,582	480	1,757	2,557	485	4,355	287	0,123
3,3-Dimethylindoleninyl	281,915	2,322	534	1,708	2,275	545	4,397	282	0,086
5-Methoxythieno[2,3-d]thiazo	436,991	1,940	639	1,380	—	—	—	—	—
5-Phenylthieno[2,3-d]thiazolyl	507,609	1,971	629	1,712	1,943	638	3,092	361	0,178
5-Bromothieno[2.3-d]thiazolyl	—	2,030	610	1,378	2,030	610	—	—	0,034
6-Bromothieno[2,3-d]thiazolyl	—	2,066	600	1,361	—	—	—	—	—
6-Methoxythieno[2,3-d]thiazolyl	426,080	2,065	601	1,631	—	—	—	—	—
Benzothiazolyl	344,834	2,250	551	1,530	2,215	559	3,974	312	0.034
5-Nitrobenzothiazolyl	485,466	2,254	550	1,652	2,200	560	—	—	—
5-Phenylbenzothiazolyl	—	2,206	562	1,468	1,187	567	—	—	—
5-Methoxybenzothiazolyl	426,052	2,168	572	1,484	2,153	576	—	—	—
4-Nitrobenzothiazolyl	485,604	2,145	578	1,756	2,130	582	—	—	—
4-Aminobenzothiazolyl	422,607	2,202	563	1,724	2,191	566	—	—	—
6-Methoxybenzothiazolyl	426,086	2,178	570	1,677	2,17	574	—	—	—
6-Phenylbenzothiazolyl	510,184	2,148	577	1,769	2,16	574	—	—	—
6-Styrylbenzothiazolyl	544,130	2,093		1,568	2,08	595	—	—	—
Benzothiazolyl with R = $N(C_2H_5)_2$	382,311	2,630	471	1,378	2,644	462	3,647	340	0,034
Benzothiazolyl with R = CN	373,029	2,033	610	1,371	2,00	620	3,435	361	0,024
6-Diethylaminobenzothiazolyl	425,587	1,993	622	0,456	2,00	620	3,285	347	0,654
6-Nitrobenzothiazolyl	419,054	2,140	578	1,548	2,120	585	3,90	318	0,123

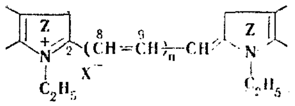
TABLE 2. Energy and Spectral Characteristics of Dyes with the II Structure

Z' in formula II	$-E_{tot}$, eV	$E^{th}_{0\to 1}$		$f_{0\to 1}$	$E^{exp}_{0\to 1}$	
		eV	nm		eV	nm
4-Pyridyl	227,183	2,091	593	1,687	2,060	602
4-Quinolyl	333,778	1,774	699	1,789	1,744	711
Thieno[2,3-b]-4-pyridyl	343,795	1,940	639	1,791	1,938	640
Furo[3,2-b]-4-pyridyl	—	2,030	610	—	2,013	616
Selenophenol[2,3-b]-4-pyridyl	—	2,000	620	—	1,987	624

group, and the β integrals and lengths of the corresponding bonds (i.e., C-N and N-O) were borrowed from [10]. The β integrals for these bonds were not varied during the calculation, and the bond lengths were not recalculated. The ionic forms of the dyes, which have a symmetrical structure (with a removed electron) were calculated. The interaction of 30 excited configurations with the lowest energies was taken into account in the calculation of the energies of the singlet—singlet π—π* transitions. The distribution of the electron densities and the bond orders in the lowest excited singlet states were calculated with allowance for the interaction of the configurations. In addition to the energy characteristics, the reactivity indices were also calculated. The results of the calculations are presented in Tables 1-5.

Analysis of the data in Tables 1 and 2 shows that in the case of thieno-2-thiazolyl and thieno-, furo-, and 6-pyridylcarbocyanines less energy is necessary for transition to the first excited singlet state ($^1S_1$) than for the benzothiazolyl and 2-quinolyl derivatives. A higher excitation energy is characteristic for dyes with thieno[2,3-b]-4-pyridyl residues than for quino-4-carbocyanine. The dyes that are selenopheno- and furo[2,3-b]-4-pyridyl derivatives are characterized by higher excitation energies than thieno-4-pyridylcarbocyanine.

TABLE 3. Reactivity Indices of the Polymethylidyne Dyes



Z	n	$-E_{\pi_B}$	pK_a	$f_E{}^a(C_8)$	$f_N{}^a(C_2)$	$F^a{}_{C_8}$	$F^a{}_{C_9}$
Benzothiazolyl	0	21,467	—	0,346	0,613	—	0,450
Benzothiazolyl	1	24,411	−0,62	0,380	0,433	0,456	0,470
Benzothiazolyl	2	27,111	0,42	0,390	0,432	0,464	0,472
2-Quinolyl	1	27,081	1,41	0,401	0,427	0,467	0,476
Thieno[2,3-d]thiazolyl	1	12,923	0.80	0,394	0,434	0,464	0,473
Thiazolyl	1	8,629	2,37	0,417	0,430	0,457	0,470
5-Phenylthiazolyl	1	30,448	1.04	0,278	0,407	0,459	0,469
4-Phenylthiazolyl	1	30,299	1.7	0,307	0,428	0,458	0,469
5-β-Nitrovinylthiazolyl	1	—	—	0,327	0,402	0,453	0,476
4-β-Nitrovinylthiazolyl	1	—	—	0,383	0,432	0,454	0,473
5-α-Methoxyvinylthiazolyl	1	—	—	0,380	0,423	0,453	0,474
6-Phenylbenzothiazolyl	1	46,313	−0,70	0,290	0,432	0,457	0,469
6-Acetamidobenzothiazolyl	1	35.788	−0,70	0,289	0,427	0,457	0,470
6-Aminobenzothiazolyl	1	26,867	−1,26	0,212	0,418	0,461	0,465
6-Carboxybenzothiazolyl	1	—	−1,24	0,368	0,432	0,454	0,473
5-Aminobenzothiazolyl	1	26,867	−1,19	0,266	0,431	0,458	0,468
7-Aminobenzothiazolyl	1	26,730	—	0,151	0,431	0,458	0,467

a) The atoms of the external polymethylidyne chain of the carbocyanines with the maximum reactivity indices are indicated.

A rather high degree of nonuniformity of the distribution of the π charge on the atoms and an appreciable difference in the bond orders in both the polymethylidine chromophore and in the azole rings of the heteroresidues are common to all of the cyanines with I and II structures in the ground singlet state ($^1S_0$). The considerable negative charge of the carbon atom in the α position of the external polymethylidyne chain of the carbocyanines corresponds to their ability to undergo protonation in this position. The boundary electron density ($f_E{}^{11}$) increases on passing from thia- to quino-2-carbocyanine and from the benzothiazole and quinoline derivatives to thienothiazolo- and thienopyridocarbocyanines (Table 3). This indicates an increase in the tendency of cyanines to undergo attack by electrophilic reagents on passing to derivatives of more basic heterocycles. If one judges from the $f_N{}^{11}$ values, both the atom in the 2 position of the azole ring of the heteroresidue and the meso carbon atom of the external chain may be subjected to the action of nucleophilic reagents. The f_N value which characterizes this capacity, decreases on passing from monomethylidyne to trimethylidynecyanines and dyes with residues from more basic heterocycles. In conformity with the F^{11} values, all of the carbon atoms of the external polymethylidyne chain of the cyanines are capable of undergoing reaction with radical reagents. The bond orders show that the weakest bonds at high temperatures in carbocyanines that are 1,3-azole derivatives should be the 6—7 (7-8) and 2-3 (2'-3') bonds and in pyrido- and quinocyanines should be the 2-7 (4-7) and 1-2 (1'-2') bonds (Tables 4 and 5).

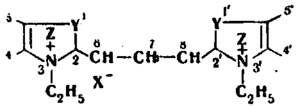
In dyes with I and II structures the most substantial distributions of π charge during long-wave excitation occur in the principal polymethylidyne chromophore; in this case the uniformity of the π-electron density distribution in it increases, the orders of the bonds between its atoms decrease, and the uniformity of the charge distribution in the azole rings of the heteroresidues increases.

The second ($^1S_2$) and higher excited singlet states differ from $^1S_0$ and $^1S_1$ with respect to a lower degree of uniformity of the electron-density distribution and, in particular, the absence of alternation of the π charge along the main chromophore of the dye.

The character of the charge distribution in the azole rings of the heteroresidues has an appreciable effect on the transition of the dye molecule to the $^1S_1$ state: the more uniform the electron-density distribution in the azole rings and the more equalized the bond orders in them, the lower the energy of the long-wave excitation; this is characteristic in particular for thiazolo and 2-pyridocarbocyanines.

The azole rings are also responsible for appreciable differences in the transmission of electronic effects of the condensed ring to the polymethylidyne chromophore. Thus the pyridinium ring is a system with more delocalized charge than five-membered 1,3-azole rings in the heteroresidues of the dyes, as a consequence of which more effective transmission of

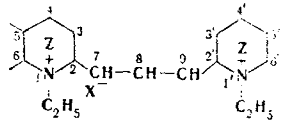
TABLE 4. Charges (q_r) and Bond Orders (p_{rs}) in



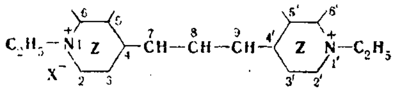
III

Z in formula III	State	q_r on the atoms							p_{rs}			
		1	2	3	4	5	6	7	6—7 (7—8)	2—6 (8—2′)	2—3 (2′—3′)	3—4 (3′—4′)
Thiazolyl	$^1S_0$	0,098	0,111	0,391	−0,031	−0,024	−0,120	0,148	0,629	0,647	0,563	0,371
Thiazolyl	$^1S_1$	0,161	−0,085	0,398	0,009	0,012	0,054	−0,097	0,588	0,618	0,476	0,428
Thieno[2,3-d]thiazolyl	$^1S_0$	0,089	0,102	0,393	−0,073	−0,041	−0,122	0,140	0,630	0,645	0,574	0,370
Thieno[2,3-d]thiazolyl	$^1S_1$	0,101	−0,093	0,405	−0,009	−0,015	0,018	−0,086	0,599	0,622	0,475	0,446
5-Styrylthiazolyl	$^1S_0$	0,090	0,092	0,399	−0,061	−0,020	−0,121	0,133	0,630	0,644	0,562	0,388
5-Styrylthiazolyl	$^1S_1$	0,084	−0,089	0,404	0,003	−0,017	0,018	−0,079	0,601	0,636	0,476	0,459
5-Phenylthieno[2,3-d]thiazolyl	$^1S_0$	0,087	0,096	0,395	−0,082	−0,030	−0,124	0,134	0,630	0,643	0,564	0,374
Benzothiazolyl	$^1S_0$	0,077	0,124	0,382	−0,058	−0,050	−0,122	0,151	0,630	0,648	0,576	0,326
Benzothiazolyl	$^1S_1$	0,107	−0,073	0,400	−0,017	−0,025	0,049	−0,096	0,594	0,620	0,491	0,393
Benzoxazolyl	$^1S_1$	0,241	−0,085	0,374	−0,037	−0,017	0,056	−0,134	0,595	0,559	0,464	0,408
1-Ethylbenzimidazolyl	$^1S_1$	0,235	−0,071	0,249	−0,008	−0,010	0,062	−0,114	0,588	0,635	0,367	0,299
6-Aminobenzothiazolyl	$^1S_0$	0,068	0,103	0,403	−0,106	−0,031	−0,132	0,132	0,632	0,636	0,593	0,330
5-Aminobenzothiazolyl	$^1S_0$	0,071	0,120	0,398	0,052	−0,089	−0,121	0,149	0,633	0,640	0,588	0,331
6-Nitrobenzothiazolyl	$^1S_1$	0,110	−0,057	0,422	−0,008	−0,021	0,074	−0,085	0,596	0,612	0,507	0,406
5-Nitrobenzothiazolyl	$^1S_1$	0,109	−0,065	0,410	−0,025	−0,007	0,048	−0,095	0,595	0,612	0,506	0,397
6-Methoxybenzothiazolyl	$^1S_1$	0,073	−0,089	0,406	−0,034	−0,024	0,004	−0,098	0,598	0,634	0,492	0,404
5-Methoxybenzothiazolyl	$^1S_0$	0,071	0,121	0,397	−0,054	−0,076	−0,123	0,146	0,631	0,642	0,587	0,331
Benzothiazolyl	$^1S_2$	0,237	−0,084	0,319	−0,059	−0,013	−0,129	−0,086	0,589	0,675	0,459	0,332

TABLE 5. Charges (q_r) and Bond Orders (p_{rs}) in



IV



Formula	Z in formula IV or V	State	q_r on the atoms								p_{rs}			
			1	2	3	4	5	6	7	8	7—8 (8—9)	2—7 (9—2')	2—3 (2'—3')	1—2 (2'—1')
IV	2-Pyridyl	$^1S_0$	0,416	0,066	−0,013	0,097	−0,007	0,049	−0,163	0,112	0,645	0,587	0,513	0,447
	2-Pyridyl	$^1S_1$	0,379	−0,077	0,060	0,035	0,011	0,056	0,073	−0,073	0,609	0,552	0,529	0,389
IV	2-Quinolyl	$^1S_0$	0,293	0,100	−0,028	0,117	−0,030	0,006	−0,121	0,124	0,639	0,607	0,519	0,438
	2-Quinolyl	$^1S_1$	0,276	−0,026	0,028	0,041	−0,001	0,015	0,096	−0,044	0,617	0,551	0,556	0,373
IV	Thieno[2,3-b]pyridyl	$^1S_0$	0,306	0,076	−0,017	0,112	−0,042	−0,006	−0,124	0,064	0,618	0,587	0,541	0,429
	Thieno[2,3-b]pyridyl	$^1S_1$	0,281	−0,061	−0,043	0,031	−0,019	0,011	0,088	−0,099	0,617	0,554	0,556	0,351
IV	Furo[2,3-b]pyridyl	$^1S_0$	0,297	0,079	−0,011	0,115	−0,036	−0,022	−0,116	0,073	0,614	0,596	0,538	0,422
IV	2-Quinolyl	$^1S_2$	0,328	0,091	−0,064	0,022	−0,014	0,001	0,028	0,125	0,638	0,485	0,601	0,445
V	4-Pyridyl	$^1S_0$	0,332	0,064	0,008	0,100	0,008	0,061	−0,097	0,105	0,643	0,592[a]	0,491[b]	0,441
	4-Pyridyl	$^1S_1$	0,322	0,015	0,024	−0,016	0,024	0,015	0,142	−0,074	0,612	0,524	0,495	0,410
V	4-Quinolyl	$^1S_0$	0,383	0,066	−0,061	0,106	−0,033	−0,006	−0,092	0,112	0,638	0,616	0,506	0,514
	4-Quinolyl	$^1S_1$	0,390	−0,011	0,004	−0,025	−0,002	−0,003	0,121	−0,068	0,611	0,561	0,506	0,491
V	Thieno[2,3-b]-4-pyridyl	$^1S_0$	0,406	0,039	−0,033	0,093	−0,025	0,006	−0,106	0,102	0,641	0,608	0,495	0,497
V	Furo[2,3-b]pyridyl	$^1S_0$	0,306	0,062	−0,015	0,105	−0,047	0,001	−0,088	0,110	0,639	0,608	0,492	0,434

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[a] Orders of the 4-7 (9-4') bonds. [b] Orders of the 3-4 (3'-4') bonds.

the electronic effects of the condensed ring through it to the chromophore is possible, and this is responsible for the differences in the colors of thia-, oxa-, and quino-2-cyanines.

Annelated five-membered rings in the heteroresidues of thieno- and furothiazoles and -pyridines display greater electron-donor abilities than condensed benzo groups, and this gives rise to an increase in the π-electron density and uniformity of its distribution in the chromophore and azole rings.

A characteristic peculiarity of pyrido-4-carbocyanine is the inclusion of a considerable portion of its principal polymethylidyne chromophore in the heteroresidues, in which it is branched. It has been shown [12] that the introduction of an aromatic ring in the external polymethylidyne chain of thiacarbocyanine causes a significant increase in the excitation energy due to branching of the chromophore. It follows from Tables 1 and 2 that on passing from pyrido-2- to pyrido-4-carbocyanine the absorption maximum is shifted only 42 nm to the long-wave region of the spectrum, although in this case the polymethylidyne chromophore is lengthened by two vinylene groups, which usually gives rise to a considerably larger bathochromic shift. The results of the calculations show that the principal polymethylidyne chromophore of pyrido-4-carbocyanine differs from the chromophore of the 2-pyridyl derivative with respect to the character of the electron-density distribution in the various states. On passing to the $^1S_1$ state the uniformity of the electron-density distribution in its chromophore increases, but, in contrast to the dyes with I structures, complete alternation of the π charge is not achieved in it. The presence of a positive charge on most of the atoms of the pyridine rings evidently impairs the conjugation of the π electrons along the entire chromophore; this is probably the reason for the considerable decrease in the bathochromic shift as compared with the shift that might have been expected as a result of its lengthening on passing from pyrido-2- to pyrido-4-carbocyanine. When benzo groups are introduced in the 5,6 and 5',6' positions of the latter dye, the electron density in the pyridine rings and the uniformity of its distribution increase, particularly along the branch of the chromophore, the carbon atoms of the pyridine rings of which and the annelated benzo groups are not shared; this reduces the effect of branching of the chromophore. It follows from an analysis of the results of the calculations that the lower bathochromic shift when thiophene and furan rings, respectively, are incorporated in the same positions of pyrido-4-carbocyanine is due to the greater possibility of transmission of conjugation over both branches of the chromophore in the pyridine rings of the heteroresidues of these dyes.

Lengthening of the polymethine chain of the cyanines leads to an increase in the bond orders and equalization of the π-electron-density distribution in the principal chromophore in both the $^1S_0$ and $^1S_1$ states.

It follows from an analysis of the data in Table 1 that electron-donor and electron-acceptor groups lower the energy of the transition from the $^1S_0$ state to the $^1S_1$ state when they are introduced in the 5,5' position of thiazolo- and thienothiazolocyanines and in the 6,6' position of thiacarbocyanines. Electron-donor substituents in the 5,5' positions of thiacarbocyanine also lower the excitation energy, while electron-acceptor groups cause only a slight increase in the excitation energy.

Appreciably lower energy of the transition to the $^1S_1$ state than for the corresponding 6,6' derivatives of thienothiazole is characteristic for 5,5'-disubstituted thieno[2,3-d]-thiazolocarbocyanines. Both electron donors and acceptors in the 5,5' positions of thiazolocarbocyanines also have an appreciably greater effect on the decrease in the excitation energy than in the analogous 4,4'-disubstituted dyes.

Analysis of the data in Table 4 shows that electron-donor substituents in the heteroresidues of the dyes with I structures as a rule increase the electron density in the chromophore and azole rings. To a greater or lesser degree (depending on the position in the heteroresidues) these groups increase the uniformity of the electron-density distribution both along the chromophore and in the azole rings. Electron-acceptor groups in 6,6'-disubstituted thiacarbocyanines also appreciably increase the uniformity of the electron-density distribution in the polymethylidyne chromophore, whereas when they are in the 5,5' positions they lower the electron density in the thiazole rings and have little effect on the character of its distribution in the chromophore. This is probably the reason for their slight effect on the color of these dyes.

When both electron acceptors and donors are introduced in the 5,5' positions of thiazolo- and thienothiazolocarbocyanines, they lead to a more uniform electron-density distribution in the chromophore than in the corresponding 4,4'- and 6,6'-disubstituted dyes. A more uniform distribution of the π charge in the principal chromophore than in 4,4'-disubstituted dyes is also characteristic for 5,5'-diphenyl- and 5,5'-distyrylthiazolocarbocyanines.

Substituents in 5,5'-substituted thienothiazolocarbocyanines give rise to a considerable change in the electron density of the carbon atoms and have only a slight effect on the charge on the sulfur atoms of the condensed thiophene rings. Consequently, the electronic effects of the substituents in the chromophores in these dyes are transmitted along the system of more labile electrons of the π electrons of the thiophene rings, and this is probably responsible for the lower energies of the long-wave excitation of the dyes that are derivative of 5-substituted thienothiazoles as compared with the corresponding cyanines with residues of 6-substituted benzothiazoles and the small differences in the excitation energies in the case of 5,5'-distyrylthiazolo- and 5,5'-diphenylthieno[2,3-d]thiazolocarbocyanines. These two cyanines are similar with respect to the character of the electron-density distribution in the thiazole rings and the chromophore.

It is apparent from the data in Table 4 that in the $^1S_0$ state substituents in various positions of the heteroresidues of thiazolo-, thia-, and thienothiazolocarbocyanines cause significant changes in the electron density on the carbon atoms of the thiazole rings but have only a slight effect on the charge on their sulfur atoms. At the same time, considerable changes in the charges on the sulfur atoms of the thiazole rings as a function of the character of the substituents and their position in the heteroresidues are characteristic for the $^1S_1$ state. The uniformity of the electron-density distribution in the thiazole rings increases when electron-donor groups are introduced in the heteroresidues of the dyes with the I structure in the $^1S_1$ state (and in the $^1S_0$ state); a greater increase is observed on the sulfur atoms, except for 5,5'-disubstituted thiacarbocyanines, for which a greater increase on the nitrogen atoms is characteristic. Electron-acceptor groups change the magnitude of the π charge of the sulfur atoms only slightly and increase the positive charge of the nitrogen atoms somewhat. In addition, in the 5,5' positions of thiacarbocyanines these substituents cause considerable redistribution of the π charges in the condensed benzene rings. Phenyl and styryl groups in the 5,5' positions of thiazolocarbocyanines increase the electron density on the sulfur atoms, and the same groups in the 4,4' derivatives increase the electron density on the nitrogen atoms.

Strong electron-donor groups in the meso position of the polymethylidyne chain of thiacarbocyanine increase the excitation energy and decrease the uniformity of the electron-density distribution in the main chromophore and equalization of the bond orders in it; this corresponds to a shift in the absorption maxima of these dyes to the short-wave region of the spectrum. Strong electron-acceptor groups give rise to the reverse effect.

The data in Table 3 show that substituents introduced in the heteroresidues of polymethylidyne dyes cause substantial changes in the reactivity indices and consequently affect their ability to undergo reaction with electropositive and electronegative reagents, particularly silver ions.

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