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Abstract

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Dipole Moments of Some Merocyanine Dyes Derived from Rhodanine

The dipole moments of merocyanine dyes have been little studied ($^{1-3}$). Kushner and Smyth (^{1}) only showed that the dipole moments of merocyanines increase greatly with a sharp increase in the electron-donor and, correspondingly, electron-acceptor character of the nitrogenous and ketomethylene residues entering into the composition of the dyes.

We have measured, by the heterodyne method in benzene at 25°, the dipole moments of dimethinemerocyanines—derivatives of 3-ethylrhodanine containing various nitrogenous heterocyclic residues. In connection with the low solubility of the N-ethylates of some merocyanines, the corresponding N-*n*-butyl derivatives were investigated; moreover, for the dye with a benzoxazole residue it was shown that replacement of the ethyl group by an *n*-butyl group does not substantially affect the magnitude of the dipole moment. In addition to the dipole moments of dyes 1-10, the dipole moments of 3-ethylrhodanine (12), 1-ethyl-3,3-dimethyl-2-methyleneindoline (13), and monomethineoxanine betaine (11) were also measured.

The merocyanines were obtained by known methods (^{4,7}), and the monomethineoxanine betaine (11) by hydrolysis of the quaternary salt formed by the action of dimethyl sulfate on the monomethineoxanine derivative of 3-ethylrhodanine.

The dyes were purified by chromatography on alumina followed by crystallization from ethyl alcohol, and then from benzene, and were dried in vacuum at 80°. Compounds 12 and 13 were distilled in vacuum before investigation.

The results of the measurements are given in Table 1, where the numbering, formulas, concentration limits in mole fractions, and polarizations $P_{\text{obs}}, P_{\text{el}}, P_{\text{orient}}, P_{\text{el}}$ are listed in sequence, calculated from the relationships.

The data presented show that the dipole moments of compounds 12 and 13, which enter into the composition of dye 1, are small (1.75 and 1.13 D).

The dipole moments of the free heterocyclic bases (thiazole 1.64 (^{5}), benzthiazole 1.45 (^{5}), benzoxazole 1.47 (^{6})) are also very small.

Thus, each of the residues contributes from 1 to 2 D to the moment, whereas the moments of the merocyanine molecules range from 6.3 to 9.9 D. This observation is a vivid illustration of the conjugation of the nitrogen of the heteroresidues with the carbonyl oxygen of ethylrhodanine. Comparison of the magnitudes of the dipole moments and the hypsochromic shifts of the absorption maximum of the dyes relative to the calculated values ([4,7,8]) shows that there is a definite correspondence between these quantities. At the same time, taking into account the relative basicity of the residues of indolenine, benzimidazole, or pyridine ([4,7]), one could have expected larger values

Table 1

No.	Formula	f	P_{total}	P_{el}	P_{or}	Dipole moment $\mu \cdot 10^{18}$
1	Structural formula: N-ethyl heterocyclic residue with $C(CH_3)_2$, linked through $= CHCH =$ to an N-ethyl rhodanine residue	0,000744 0,00109	921,96	104,24	817,72	6,27

No.	Formula	f	P_{total}	P_{el}	P_{or}	Dipole moment $\mu \cdot 10^{18}$
2	Structural formula: N-butyl benzothiazole residue, linked through $= CH - CH =$ to an N-ethyl rhodanine residue	0,0005650,000839	1334,77	107,54	1227,23	7,68
3	Structural formula: N-*n*-butyl benzoxazole residue, linked through $= CH - CH =$ to an N-ethyl rhodanine residue	0,000650,00109	1506,84	101,21	1405,63	8,22

No.	Formula	f	P_{total}	P_{el}	P_{or}	Dipole moment $\mu \cdot 10^{18}$
4	Structural formula: N-ethyl benzoxazole residue, linked through $= CH - CH =$ to an N-ethyl rhodanine residue	0,000970,00111	1551,31	91,95	1459,36	8,37

No.	Formula	f	P_{total}	P_{el}	P_{or}	Dipole moment $\mu \cdot 10^{18}$
5	Structural formula: benzimidazole residue with $N-CH_3$ and $N-C_2H_5$, linked through $=CH-CH=$ to an N-ethyl rhodanine residue	0,000056 0,000059	2139,75	98,2	2041,55	9,9

No.	Formula	f		P_{total}	P_{el}	P_{or}	Dipole moment $\mu \cdot 10^{18}$
6	Structural formula: saturated thiazoline residue with H_2C, H_2C, S, and $N-C_2H_5$, linked through $=CH-CH=$ to an N-ethyl rhodanine residue	0,00166	0,00171	1639,47	83,30	1556,12	8,6

No.	Formula	f	P_{total}	P_{el}	P_{or}	Dipole moment $\mu \cdot 10^{18}$
7	Structural formula: saturated pyrroline residue with H_2C-CH_2, H_2C, and $N-C_2H_5$, linked through $=CH-CH=$ to an N-ethyl rhodanine residue	0,00078 0,00146	1585,97	79,98	1505,99	8,51

No.	Formula	f		P_{total}	P_{el}	P_{or}	Dipole moment $\mu \cdot 10^{18}$
8	Structural formula: thiazole residue with HC, HC, S, and $N-C_2H_5$, linked through $=CH-CH=$ to an N-ethyl rhodanine residue	0,00022	0,00047	1835,26	82,8	1752,46	9,18
9	Structural formula: N-ethyl pyridine residue, linked through $C=CH-CH=$ to an N-ethyl rhodanine residue	0,00058	0,00101	1825,81	83,77	1742	9,15

Table 1 (continued)

No.	Formula	f		P	P	P	Dipole moment, $\mu \cdot 10^{18}$
10	Structural formula: N-ethyl quinoline residue connected through $-$CH $=$ CH$-$ to an N-ethyl rhodanine residue	0,000338	0,000425	1380,99	98,4	1282,59	7,85
11	Monomethinoxanine-betaine. Structural formula: substituted thiazolium-betaine residue connected through $-$CH $=$ to an N-ethyl rhodanine-type residue	0,000790	0,00019	1133,97	83,17	1050,8	7,11

No.	Formula	f	P	P	P	Dipole moment, $\mu \cdot 10^{18}$
12	3-Ethylrhodanine. Structural formula: *N*-ethyl rhodanine	0,004250,01214	105,79	42,19	63,60	1,75
13	1-Ethyl-3,3-dimethyl-2-methyleneindoline. Structural formula: 1-ethyl-3,3-dimethyl-2-methyleneindoline	0,0137	86,46	60,02	26,44	1,13

dipole moments for dyes derived from the last two bases.

These deviations are evidently associated with the direction of the moment vectors of the hetero-residues, the magnitudes and directions of which cannot yet be calculated with sufficient accuracy.

The decrease in the magnitude of the dye moments when the thiazole (8) or pyridine (9) residue is replaced, respectively, by a benzothiazole (2) or quinoline residue (10), is explained by additional conjugation of the nitrogen atom with the benzene ring, as a result of which a moment appears that is directed in the opposite direction.

The moment of dye 7 gives an overall measure of the polarity caused by conjugation of the nitrogen atom with 3-ethylrhodanine through the polymethine chain.

Comparison of the moments of dyes 6 and 7 shows the small role of the sulfur atom of the hetero-residue in conjugation.

However, the closeness of the moment values of these dyes may also be due to other causes. The moments of dyes with benzothiazole (2) and benzoxazole (3) residues differ substantially from one another, whereas the moments of the corresponding initial bases practically coincide ($1,45$ and $1,47$ D).

It is interesting that these dyes likewise differ from one another in the magnitudes of the hypsochromic shifts of the absorption maximum ([4,7,8]).

In the case of compound 11, i.e., a bipolar ion, one might have expected a larger value of the dipole moment. As in certain other cases, it turns out that although the moments of bipolar ions are considerable, they are nevertheless smaller than the expected values.

It is possible that the electrostatic attraction of the charges hinders their delocalization and promotes their maximum convergence.

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Note: Figure translations are in progress. See original paper for figures.