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Abstract

Full Text

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DIPOLE MOMENTS OF MEROCYANINES DERIVED FROM IMIDAZOLIDINEDIONE-(2,4) AND ITS THIO- AND DITHIO-SUBSTITUTED ANALOGS

In continuation of our previous work ([1,2]), we measured in benzene at 25° the dipole moments of the following eight substances:

1) 1,3-dimethylthiohydantoin, 2) 1-methyl-3-ethylthiohydantoin, 3) 1-phenyl-3-ethylthiohydantoin, 4) 1-phenyl-3-ethyl-5(3′-ethylbenzthiazolinylidene-2′-ethylidene)-imidazolidinthion-(4)-one-(2), 5) 1-phenyl-3-ethyl-5(3′-ethylbenzthiazolinylidene-2′-ethylidene)-imidazolidinthion-(2)-one-(4), 6) 1-methyl-3-ethyl-5(3′-ethylbenzthiazolinylidene-2′-ethylidene)-imidazolidinthion-(2)-one-(4), 7) 1-phenyl-3-ethyl-5(3′-ethylbenzthiazolinylidene-2′-ethylidene)-imidazolidinedione-(2,4), 8) 1-phenyl-3-ethyl-5(3′-ethylbenzthiazolinylidene-2′-ethylidene)-imidazolidinthione-(2,4).

Table 1 gives, in sequence, the structural formulas, molar fractions of the substances studied in benzene, the total polarization (P_{tot}), the electronic polarization (P_{el}), the orientational polarization (P_{or}), the dipole moment in debyes, and, for the dyes, the absorption maximum (λ_{max}) in ethyl alcohol (in mμ).

The close values of the moments of 1 and 2 are quite natural. The lowered value of the moment of 3 as compared with 2 can be explained by the fact that, in the ortho and para positions of the phenyl group, a small negative charge appears, directed opposite to the negative end of the dipole of the $C = O$ bond. We note that the moments of molecules 4 and 5 are equal. In case 4, the negative charge on the sulfur atom appears through conjugation with the nitrogen atom of the benzthiazole residue, and also through conjugation with the neighboring nitrogen atom. The oxygen in this molecule is partially negatively charged through conjugation with two neighboring nitrogen atoms. In compound 5, the oxygen is conjugated with the left-hand part of the molecule and with the neighboring nitrogen atom. The sulfur, however, in this case is conjugated with two neighboring nitrogen atoms. Apparently, in both cases the system is equally polar, and the dipole moment does not reflect the fact that sulfur is usually considered more electropositive than oxygen.

Of interest is the considerable increase in the moment of substance 8 as compared with 7, by 3.3 D. Since it is usually assumed that sulfur is more electropositive than oxygen, one might seemingly have expected the opposite course of the moments. The moment of the $C = O$ bond is 2.3 (if the moment of the CH bond is taken as 0.4). The moment of the $C = S$ bond is correspondingly 2.6, i.e., only slightly larger. This does not yet mean that the electronic displacements in the $C = S$ grouping are greater, since the length of the $C = S$ bond is approximately 0.5 Å greater than that of the $C = O$ bond. Apparently, conjugation with sulfur is much greater than with oxygen; moreover, sulfur is the negative end of the dipole, and nitrogen in the $\sigma^3\pi$ state is the positive end. Although oxygen is considered more electronegative than sulfur, the dipole moment of substance 8 is greater by 3.3 D. The onium states of the three nitrogen atoms sharply suppress the oxonium state of oxygen and the sulfonium state of sulfur. Therefore the decisive role is played by the electron affinity of these atoms, and it, as is known, is greater for sulfur (2.07 eV) than for oxygen (1.48 eV). Probably in connection with this, a larger effective charge appears on sulfur in 8.

Table 1

No.	Substance	Molar fractions	P_{tot}	P_{el}	P_{or}	Dipole moment $m_0 \cdot 10^{18}$, D	Absorption maximum $\lambda_{\max}$, mμ
1	Imidazolidinethione derivative: ring with H_2C, $N{-}CH_3$, $N{-}CH_3$, C=O, C=S	0.00078–0.00165	177.3	38.1	139.2	2.59	
2	Imidazolidinethione derivative: ring with H_2C, $N{-}CH_3$, $N{-}C_2H_5$, C=O, C=S	0.00047–0.00142	187.2	42.7	144.5	2.63	

No.	Substance	Molar fractions	P_{tot}	P_{el}	P_{or}	Dipole moment $m_0 \cdot 10^{18}$, D	Absorption maximum λ_{max}, mμ
3	Imidazolidinone-thione derivative: ring with H_2C, $N-C_6H_5$, $N-C_2H_5$, C=O, C=S	0.00016–0.00192	176.6	63.3	114.3	2.34	
4	Merocyanine dye: benzothiazoline residue $N-C_2H_5$, conjugated chain C=CH−CH=C, imidazolidinone-thione residue with $N-C_6H_5$, $N-C_2H_5$, C=S, C=O	0.00009–0.00010	1238	118.4	1119.6	7.34	569

No.	Substance	Molar fractions	P_{tot}	P_{el}	P_{or}	Dipole moment $m_0 \cdot 10^{18}$, D	Absorption maximum $\lambda_{\max}$, mμ
5	Merocyanide dye: benzothiazoline residue $N{-}C_2H_5$, conjugated chain $C{=}CH{-}CH{=}C$, imidazolidinonethione residue with $N{-}C_6H_5$, $N{-}C_2H_5$, $C{=}O$, $C{=}S$	0.00009–0.00018	1250	118.4	1131.6	7.35	512

No.	Substance	Molar fractions	P_{tot}	P_{el}	P_{or}	Dipole moment $m_0 \cdot 10^{18}$, D	Absorption maximum $\lambda_{\max}$, mμ
6	Merocyanine dye: benzothiazoline residue $N{-}C_2H_5$, conjugated chain $C{=}CH{-}CH{=}C$, imidazolidinonethione residue with $N{-}CH_3$, $N{-}C_2H_5$, $C{=}O$, $C{=}S$	0.00018–0.00025	875.9	98.8	777.1	6.11	520

No.	Substance	Molar fractions	P_{tot}	P_{el}	P_{or}	Dipole moment $m_0 \cdot 10^{18}$, D	Absorption maximum $\lambda_{\max}$, mμ
7	Merocyanine dye: benzothiazoline residue $N{-}C_2H_5$, conjugated chain $C{=}CH{-}CH{=}$, imidazolidinedione residue with $N{-}C_6H_5$, $N{-}C_2H_5$, two $C{=}O$ groups	0.00026–0.00018	759	111.2	637.8	5.54	462

No.	Substance	Molar fractions	P_{tot}	P_{el}	P_{or}	Dipole moment $m_0 \cdot 10^{18}$, D	Absorption maximum λ_{max}, mμ
8	Merocyanine dye: benzothiazoline residue N−C_2H_5, conjugated chain C=CH−CH=, imidazolidinedithione residue with N−C_6H_5, N−C_2H_5, two C=S groups	0.00010–0.00011	1749	125.4	1623.6	8.83	607

The absorption spectra of the indicated dyes in the visible region were also studied. As can be seen from the data in Table 1, replacement in these merocyanines of oxygen atoms in the imidazolidinedione residue by sulfur atoms causes not only an increase in the dipole moment but also, as in the case of thiazolidine derivatives ([3,4]), leads to a considerable deepening of the color of the dyes. A particularly large bathochromic effect (95 and 107 mμ) is observed when a sulfur atom enters the 4-position of the imidazolidinedione-(2,4) residue, i.e., at the carbon atom bounding the principal polymethi-

new chromophore. It is interesting that replacement of the first oxygen atom by a sulfur atom produces a noticeably greater bathochromic effect than replacement of the second, irrespective of whether it enters the 2- or the 4-position of the imidazolidinedione-(2,4) residue (shifts of the absorption maximum, respectively, 50 and 38 mμ, 107 and 95 mμ). Evidently, the color of these dyes is significantly affected by the degree of conjugation of the nitrogen atom in the 3-position with the groupings in positions 2 and 4.

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