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E. A. Shott-Lvova, Corresponding Member of the Academy of Sciences of the USSR Ya. K. Syrkin,

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Abstract

Full Text

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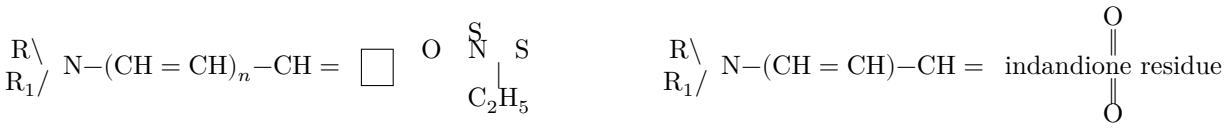
E. A. Shott-Lvova, Corresponding Member of the Academy of Sciences of the USSR Ya. K. Syrkin,
I. I. Levkoev, and M. V. Deichmeister

DIPOLE MOMENTS OF HEMIOXANINES DERIVED FROM 3-ETHYLRHODANINE AND INDANDIONE(1,3)

We have measured, by the heterodyne method in benzene at 25°, the dipole moments of a series of hemioxanines with residues of 3-ethylrhodanine (I) and indandione-1,3 (II), differing in the substituents at the extracyclic nitrogen atom and in the length of the conjugated polymethine chain,



(I) (II)

where R = C_6H_5; R_1 = HCH_3 or CH_3CO; R and R_1 together = $-(CH_2)_5$; $n = 0, 1$, or 2.

The dyes with phenylamino and phenylacetamino groups were obtained by known methods ([1–5]). By the action of piperidine on the latter in alcoholic solution, the N-piperidino derivatives were synthesized ([6]). Methylphenylaminomethylene-substituted compounds were obtained by heating 3-ethylrhodanine or indandione(1,3) with orthoformic ethyl ester and methylaniline ([7]). The dyes were purified by chromatography on aluminum oxide and subsequent crystallization from ethyl alcohol and then from benzene, and were dried in vacuum at 70–80°.

Table 1 gives, in order, the numbering, the formula of the compound, the limits of the measured concentrations, the total and electronic polarizations, the values of the dipole moments in Debye units, and the position of the absorption maximum of the alcoholic solutions of the dyes (λ_{max}), measured on an SF-4 spectrophotometer. The electronic polarizations were determined from bond refractions. Atomic polarizations were not specially taken into account, which can

introduce only insignificant changes into the magnitude of the dipole moment, since all the substances measured have a large orientational polarization.

In the compounds investigated, the extracyclic nitrogen atom is bonded to three atoms. However, the configuration in this case is probably not pyramidal, but planar, as in urea, acetamide, and other compounds in which nitrogen is to a considerable extent positively charged (with sp^2-hybridization and the formation of three σ- and one π-bond) ([8]). However, the dipole-moment method is insufficient for an unambiguous establishment of the configuration.

The experimental data show that compounds differing only in the length of the polymethine chain have sharply different moments. An increase in the number of double bonds between the polar residues $\left(>\mathrm{C}=\mathrm{O}\text{ and }-\mathrm{N}\begin{matrix}\mathrm{R}\\\mathrm{R}_1\end{matrix}\right)$ always causes an increase in the moment. This is evidently connected not only with a change in configuration, but also with an increase in the overall polarity upon lengthening of the polymethine chain. Upon introduction of one vinylene group the moment increases to a greater extent than upon introduction of a second such group ([9]). This indicates that conjugation between oxygen and the extracyclic

Table 1

No.	Formula	Molar fractions, f	P_{total}	P_{el}	Dipole moment $\mu \cdot 10^{18}$ (D)	Absorption maximum in C_2H_5OH (mμ)
1	indandione-(1,3)	0,00063	0,00325	192,4	38,2	2,72	–
2	C_6H_5NH residue with $N-C_2H_5$	0,00506	0,00624	153,6	74,5	4,27	443
3	C_6H_5NH residue with $N-C_2H_5$	0,00110	0,00179	174,5	rhodanine	82,9	5,85	483
4	C_6H_5NH residue with $N-C_2H_5$	0,00061	0,00093	173	rhodanine	91,7	6,28	538
5	$C_5H_{10}N-$ residue with $N-C_2H_5$	0,00410	0,01387	177,6	71,2	6,23	390

No.	Formula	Molar fractions, f	P_{total}	P_{el}	Dipole moment $\mu \cdot 10^{18}$ (D)	Absorption maximum in C_2H_5OH (mμ)
6	$C_5H_{10}N\cdot CH=CH-CH=$ rhodanine residue with $N-C_2H_5$	0,0067; 0,0084	70,3	80	8,17	467
7	$C_5H_{10}N-(CH=CH)_2-CH=$ rhodanine residue with $N-C_2H_5$	0,0047; 0,0034	72,2	88,8	9,00	553
8	$C_6H_5-N(CH_3)-CH=$ rhodanine residue with $N-C_2H_5$	0,0089; 0,0074	74,2	83,7	4,39	370
9	$C_6H_5-N(CH_3)-CH=CH-CH=$ rhodanine residue with $N-C_2H_5$	0,0041; 0,0036	76,2	92,5	5,06	405
10	$C_6H_5-N(CH_3)-(CH=CH)_2-CH=$ rhodanine residue with $N-C_2H_5$	0,0029; 0,0025	78,5	101,3	5,44	437
11	$C_6H_5NH-CH=$ indandione-(1,3) residue	0,0059; 0,0132	80,6	70,2	2,40	366
12*	$C_6H_5NH-(CH=CH)_2-CH=$ indandione-(1,3) residue	0,0028; 0,0097	87,7	87,7	6,31	568

Table 1 (continued)

No.	Formula	Molar fractions, f	P_{obs}	P_{el}	Dipole moment $\mu \cdot 10^{18}$ (D)	Absorption maximum in C_2H_5OH (mμ)
13	$C_5H_{10}N-CH=$ indandione-(1,3) residue	0.0035 0.00092	316.1	67.2	3.46	338

No.	Formula	Molar fractions, f	P_{obs}	P_{el}	Dipole moment $\mu \cdot 10^{18}$ (D)	Absorption maximum in C_2H_5OH (mμ)
14	$C_5H_{10}N-C(CH_3)_2-CH=$ indandione-(1,3) residue	[illegible]	897	76	6.28	432
15	$C_5H_{10}N-(CH_2-CH)_2-$ indandione-(1,3) residue	[illegible]	289.8	84.8	7.61	535
16	3-ethylrhodanine residue with $C_6H_5N(CH_3)-CH=$ substituent	0.00092	0.00277 661.1	79.1	5.29	395
17	$C_6H_5N(CH_3)-CH=$ indandione-(1,3) residue	[illegible]	217.4	75.1	2.62	353

* 2-γ-phenylaminoallylideneindandione (1,3) is very poorly soluble in benzene. The absorption maximum of this compound in ethyl alcohol is at 470 mμ. In the previous work [5] there is a misprint.

nitrogen in these compounds, with lengthening of the polymethylene chain, gradually decreases [4,10,11]. Both the magnitudes of the change in the moments and the degree of decrease of these changes depend on the structure of the amine and ketomethylene-compound residues. These quantities are appreciably larger for hemioxanines with a piperidine residue than for compounds containing a phenylamino group (compare Nos. 5, 6, 7 with 2, 3, 4 and 13, 14, 15 with 11 and 12—Table 1). This is connected with the lower basicity of the nitrogen of the phenylamino group owing to its conjugation with the benzene nucleus; in connection with this, the electronic displacements from nitrogen toward the carbonyl group in compounds with this grouping are reduced. Let us compare dyes that are derivatives of 3-ethylrhodanine with aniline and piperidine residues. In the case of the methylene derivatives (Nos. 5 and 2) the difference between the moments is 1.96 D. In the allylidene derivatives (Nos. 6 and 3) this difference is 2.32 D, and in the case of the pentadienylidene derivatives (Nos. 7 and 4) 2.72 D. Thus, on going from one to two double bonds in the external chain this difference increases by 0.36, and on going from two to three double bonds by

0.40, i.e., it increases almost linearly with the length of the polymethylene chain. To a lesser degree, with lengthening of the polymethylene chain, the moments of compounds containing a phenylacetamino group increase (Nos. 8, 9, 10). This is connected with conjugation of the nitrogen atom not only with the benzene nucleus, but also with the oxygen atom of the acetyl group. As a result of this, conjugation through the polymethylene chain is diminished.

Although the moment of indandione (1,3), 2.72 D, is greater than that of 3-ethylrhodanine (1.75 D) [12], the moments of monomethine hemioxanines are considerably smaller for derivatives of the first of these compounds. This is apparently connected with different directions of the moment vectors in 3-ethylrhodanine and indandione (1,3).

The calculation is made difficult by the absence of data on the spatial configurations of these compounds. However, upon lengthening of the chain, the magnitudes of the moments in hemioxonols derived from indandione (1,3) increase considerably more than in derivatives of 3-ethylrhodanine. Thus, when two vinylene groups are introduced into the chain of dyes with an aniline residue, the moment increases in the first case by 3.91 D and in the second by only 2.01 D, while for compounds with a piperidine residue the corresponding increases are 4.15 and 2.77 D. These data indicate the considerably greater electron-acceptor character of the indandione (1,3) residue in comparison with 3-ethylrhodanine (5, 11). However, in derivatives of indandione (1,3) as well, conjugation of the nitrogen and oxygen atoms decreases upon lengthening of the chain, since the introduction of the first vinylene group into 2-piperidylmethyleneindandione (1,3) increases the moment by 2.82 D, whereas the second increases it by only 1.33 D.

The change in the absorption spectra of the hemioxonols studied upon lengthening of their polymethine chain is in agreement with the conclusions concerning the structure of these compounds obtained from consideration of their dipole moments. Thus, upon lengthening of the chain, the color of compounds with an acetylphenylamino group deepens relatively little (by 35 and 32 mμ per vinylene group), and the moments also increase only slightly. The greatest displacement of the absorption maximum upon introduction of vinylene groups (94–104 mμ) occurs in derivatives of indandione (1,3), in which an especially significant increase in the moments is observed at the same time. In the case of phenylamino derivatives of 3-ethylrhodanine, the introduction of the first vinylene group has a noticeably greater effect on the displacement of the absorption maximum and on the change in the moment than does the second such group (70 and 55 mμ; 1.58 and 0.43 mμ). The increase in the bathochromic shift of the absorption maximum upon introduction of the second vinylene group into the chain, as compared with the first, in dyes with a piperidine residue is possibly explained by the fact that the structure of the mono- and trimethine compounds of this series in alcoholic solution is close to the inner-salt form. In the case of the less polar pentamethine derivatives, under the same conditions, a more uniform distribution of electron density apparently occurs in the chromophore, which,

as in the case of other inner-salt dyes, should lead to a displacement of the absorption maximum into the long-wavelength region (5, 11, 13).

It is of interest to compare the moments of compounds Nos. 16 and 2. In dye (No. 16) intramolecular hydrogen bonding is impossible. In compound No. 2, the hydrogen at the nitrogen atom can form a hydrogen bond with the oxygen of the rhodanine residue, since a stable six-membered ring is thereby formed. The presence of a hydrogen bond stabilizes one spatial configuration.

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