SYNTHESIS OF 2-ACYLMETHYL- AND 2-ACYLMETHYLENE-1,3-DITHIOLO[4,5-b]QUINOXALINES FROM α-ACETYLENIC KETONES

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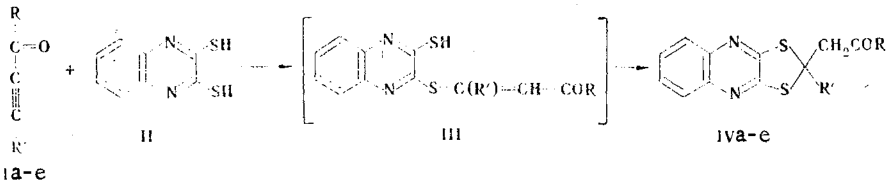
A number of 2-acylmethyl-1,3-dithiolo[4,5-b]quinoxaline derivatives were synthesized on the basis of the reaction of α-acetylenic ketones with quinoxaline-2,3-dithiol in dimethyl sulfoxide (DMSO) in the presence of K_2CO_3. Their monohydrochlorides were obtained. A new series of 2-acylmethylene-1,3-dithiolo[4,5-b]quinoxalines was obtained by the reaction of 1-bromo-2-acylacetylenes with quinoxaline-2,3-dithiol in DMSO in the presence of triethylamine.

The formation of cyclic adducts as a result of double addition to the triple bond is possible in the reaction of some dinucleophiles with acetylenic compounds [1-5].

We have investigated the reaction of α-acetylenic ketones with quinoxaline-2,3-dithiol, which proceeds via the scheme



I, IV a $R=C_6H_5$, $R'=H$; b $R=\alpha\text{-}C_4H_3S$, $R'=H$; c $R=R'=C_6H_5$; d $R=\alpha\text{-}C_4H_3S$, $R'=C_6H_5$; e $R=C_6H_5$, $R'=CH_3OCH_2$

The reaction of α-acetylenic ketones Ia-e with quinoxaline-2,3-dithiol in the case of an equimolar ratio of the reagents in dimethyl sulfoxide (DMSO) at 60°C in the presence of K_2CO_3 leads exclusively to difficult-to-obtain 2-acylmethyl-1,3-dithiolo[4,5-b]quinoxalines (IVa-e). The reaction evidently procedds through an intermediate step involving the formation of the corresponding ketovinyl sulfides (the addition of one mercapto group to the acetylenic bond) and cyclization of the latter to the corresponding IVa-e. The presence of an aryl grouping attached to the triple bond of the starting ketone facilitates the reaction, and the corresponding 2-acylmethyl-1,3-dithiolo[4,5-b]quinoxalines IVc,d are obtained in higher yields (68-78%).

At the same time, when R' = H or CH_3OCH_2, the corresponding IVa,b,e are formed in lower yields (see Table 1).

The structure of the synthesized quinoxalines IVa-e were confirmed by means of the IR and PMR spectra. In the IR spectra the absorption band of the C=O group lies at 1670-1690 cm^{-1}. The intense bands at 690-705 cm^{-1} correspond to the stretching vibrations of the C—S bond in the heteroring, while the absorption bands at 1500-1520 cm^{-1} correspond to the stretching vibrations of the C=N bond. The intense absorption band at 1445-1452 cm^{-1} corresponds to the deformation vibrations of the CH_2 group. The bands at 730-735, 1050-1080, 1420-1435, 1520-1528, and 3090-3105 cm^{-1} in the IR spectra of IVb, d correspond to the vibrations of the thiophene ring.

The PMR spectrum of IVa contains a multiplet of protons of benzene rings at 7.57 ppm, a triplet at 5.42 ppm ($^3J_{CHCH_2}$ = 7.0 Hz), which is related to the S—CH—S group, and a doublet of protons of a CH_2CO group at 3.77 ppm.

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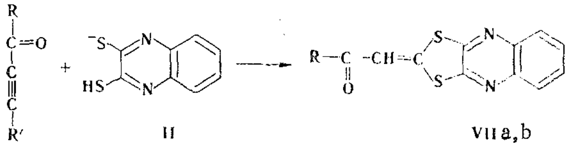
TABLE 1. 2-Acylmethyl-1,3-dithiolo[4,5-b]quinoxalines (IVa-e), Hydrochlorides (Va,b,e) and 2-Acylmethylene-1,3-dithiolo-[4,5-b]quinoxalines (VIIa,b)

Compound	mp, °C	Found, %				Empirical formula	Calc., %				Yield, %
		C	H	N	S		C	H	N	S	
IVa	153—155	63,2	3,9	8,7	19,6	$C_{17}H_{12}N_2OS_2$	63,0	3,7	8,6	19,8	70
IVb	160—162	54,7	3,2	8,4	28,5	$C_{15}H_{10}N_2OS_3$	54,6	3,0	8,5	29,1	45
IVc	214—215	68,9	4,1	6,9	15,8	$C_{23}H_{16}N_2OS_2$	69,0	4,0	7,0	16,0	78
IVd	210—212	62,1	3,6	6,7	23,7	$C_{21}H_{14}N_2OS_3$	62,1	3,5	6,9	23,6	68
IVe	114—115	61,7	4,3	7,6	17,4	$C_{19}H_{16}N_2O_2S_2$	62,0	4,3	7,6	17,4	32
Va	158—159	—	—	—	17,7	$C_{17}H_{12}N_2OS_2 \cdot HCl^a$	—	—	—	17,8	92
Vb	153—154	—	—	—	26,3	$C_{15}H_{10}N_2OS_3 \cdot HCl^b$	—	—	—	26,2	88
Ve	119—120	—	—	—	16,0	$C_{19}H_{16}N_2O_2S_2 \cdot HCl^c$	—	—	—	15,8	94
VIIa	205—207	63,5	3,2	8,5	20,1	$C_{17}H_{10}N_2OS_2$	63,4	3,2	8,7	19,9	59
VIIb	232—233	54,7	2,3	8,5	29,2	$C_{15}H_8N_2OS_3$	54,9	2,4	8,5	29,3	54

[a] Found: Cl 9.6%. Calculated: Cl 9.9%. [b] Found: Cl 9.5%. Calculated: Cl 9.6%. [c] Found: Cl 8.9%. Calculated: Cl 8.9%.

The reaction of α-bromoacetylenic ketones VIa,b with quinoxaline-2,3-dithiol in DMSO at 100°C in the presence of triethylamine leads to 2-acylmethylene-1,3-dithiolo[4,5-b]quinoxalines VIIa,b. The reaction probably proceeds via a mechanism involving direct nucleophilic substitution at the carbon atom of the triple bond [6, 7]:



VIa,b II VIIa,b

VI, VII a R=C_6H_5; b R=α-C_4H_3S

The IR spectra of VIIa,b contain absorption bands of a conjugated carbonyl group at 1630-1635 cm^{-1}, of a C=C bond at 1580-1584 cm^{-1}, of a C—S bond at 700-705 cm^{-1}, and of a C=N bond at 1510-1520 cm^{-1}. In the PMR spectrum of VIIa the signal of the olefinic proton shows up in the form of a singlet at 7.10 ppm.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions in CD_3OD or $CDCl_3$ were obtained with a Tesla BS-487-C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard.

2-Benzoylmethyl-1,3-dithiolo[4,5-b]quainoxaline (IVa). A 2 g sample of K_2CO_3 was added to a solution of 1.3 g (0.01 mole) of 1-phenylprop-2-yn-1-one (Ia) in 10 ml of DMSO, a solution of 1.94 g (0.01 mole) of quinoxaline-2,3-dithiol in 20 ml of DMSO was added dropwise with stirring, and the mixture was heated at 60°C for 2 h. It was then cooled to 20°C and poured into ice water, and the resulting precipitate was removed by filtration and recrystallized from ethanol to give 2.26 g (70%) of product. The remaining IV were similarly obtained (Table 1). Compound IVa was obtained in 64% yield in the absence of a catalyst under similar conditions.

2-Benzoylmethyl-1,3-dithiolo[4,5-b]quinoxaline Hydrochloride (Va). Dry HCl was bubbled through a solution of 0.65 g (2 mmole) of IVa in 30 ml of dry benzene at 20°C for 3 h, after which the precipitate was removed by filtration and recrystallized from ethanol to give 0.66 g (92%) of a product with mp 158-159°C. Hydrochlorides Vb,e were similarly obtained (Table 1).

2-Thenoylmethylene-1,3-dithiolo[4,5-b]quinoxaline (VIIb). A 1.01 g (0.01 mole) sample of triethylamine was added to a solution of 2.15 g (0.01 mole) of 1-(2-thienyl)-3-bromoprop-2-yn-1-one (VIb) in 20 ml of DMSO, and 1.94 g (0.01 mole) of quinoxaline-2,3-dithiol (II) was added dropwise with stirring at 20°C. After all of thiol II had been added, the mixture was heated to 100°C and stirred for 2 h. It was then cooled to 0°C, and the precipitate was removed by filtration and recrystallized from ethanol to give 1.75 g (54%) of a product with mp 232-233°C. Compound VIIa was similarly obtained (Table 1).

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ELECTRONIC STRUCTURES AND REACTIVITIES OF POLYMETHINE DYES AND THEIR DERIVATIVES

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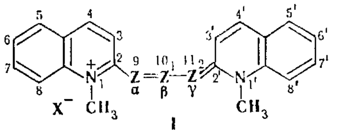
The peculiarities of the electronic structures of polymethine dyes that contain one or two nitrogen atoms in the chromophore were examined by means of the self-consistent-field (SCF) method within the Pariser–Parr–Pople (PPP) approximation as compared with the electronic structures of the corresponding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

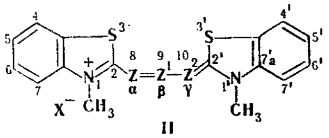
It is known that some 2-quino- and thiacarbocyanines, as well as p-dialkylaminostyryl dyes that contain nitrogen atoms in the external polymethine chain, have a pronounced desensitizing effect when they are introduced into silver halide photographic emulsions [1]. The desensitizing abilities of such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

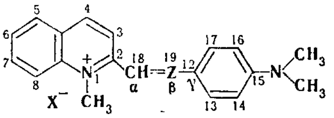
In the present communication we discuss the results of quantum-chemical calculations of the electronic structures of dyes I-III:



I



II



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).

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