RING-CHAIN TAUTOMERISM OF 3-BROMO-5-NITRO-2-HYDROXYCINNAMALDEHYDE AND ITS IMINES

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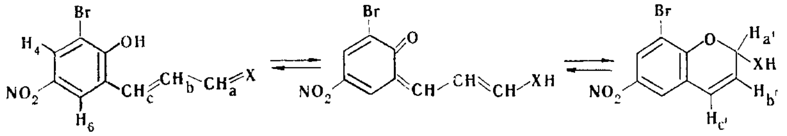
The previously undescribed 3-bromo-5-nitro-2-hydroxycinnamaldehyde and a series of its imines were synthesized. It was shown by means of the IR, UV, and PMR spectra that a cyclic 2H-chromene structure is realized in the crystalline state and in solvents with various polarities on passing from the aldehyde, which has a benzenoid structure, to its imines.

We have previously shown [1] that 5-nitro-2-hydroxycinnamaldehyde imines have a benzenoid structure in solutions in dioxane. An additional long-wave band, which was assigned to the tautomeric aci-nitro form, appears in the electronic absorption spectra of solutions of these compounds in dimethyl sulfoxide (DMSO). The extremely low solubilities made it impossible to carry out a sufficiently complete investigation of the structures of these compounds.

In the present communication we describe the preparation of the previously unknown 3-bromo-5-nitro-2-hydroxycinnamaldehyde and a series of its imines, as well as data from the electronic, vibrational, and PMR spectra of these compounds.

3-Bromo-5-nitro-2-hydroxycinnamaldehyde (I, X = O) and its O-methyl derivative were obtained by condensation of 3-bromo-5-nitrosalicylaldehyde or its methoxy derivative with acetaldehyde in an alkaline medium by the method in [2], which was used for the synthesis of 5-nitro-2-hydroxycinnamaldehyde [1]. The corresponding imines I (X = NR) are obtained in high yields when solutions of 2-hydroxy-3-bromo-5-nitrocinnamaldehyde and aromatic amines in ethanol are mixed.

The structures of the aldehyde and its imines can be represented in the form of a complex tautomeric equilibrium.



Ia Ib Ic

X=O, NR

The IR spectrum of 3-bromo-5-nitro-2-hydroxycinnamaldehyde (I, X = O) recorded in mineral oil contains bands of an associated hydroxy group (νOH) at 3170-3300 cm^{-1} and a conjugated carbonyl group (νCO) at 1670 cm^{-1}, as well as intense absorption bands of a nitro group at 1530 and 1370 cm^{-1}.

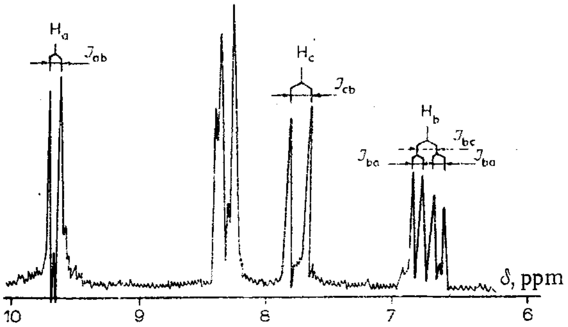


Fig. 1. PMR spectrum of 3-bromo-5-nitro-2-hydroxycinnamaldehyde (I, X = O) in DMSO.

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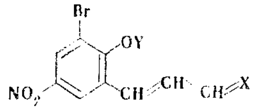
TABLE 1. Electronic Absorption Spectra of 3-Bromo-5-nitro-2-hydroxy(methoxy)cinnamaldehydes and Their Imines



X	Y	Solvent	λ_{max}, nm ($\varepsilon \cdot 10^{-3}$)
O	H	Benzene	283 (16,1)
		Dioxane	283 (15,8)
		Ethanol	285 (25,1), 395 (17,8), 420 (17,4)
		Ethanol + EtONa	285 (17,8), 418 (24,5)
		DMSO	278 (9,3), 405 (11,7), 450 (18,7)
O	Me	Dioxane	350 (28,3)
		DMSO	350 (26,7)
NPh	Me	Dioxane	370 (37,1)
		Ethanol	370 (32,7)
		DMSO	370 (27,8), 380 (26,8)
NPh	H	Dioxane	314 (12,9)
		Ethanol	250 (7,2), 314 (3,2), 400 (3,2)
		Ethanol + EtONa	245 (7,7), 300 (0,86), 400 (8,6)
		Acetonitrile	245 (10,8), 315 (13,3), 442 (3,3)
		DMSO	310 (3,6), 440 (11,6)
NC_6H_4Me-*p*	H	Dioxane	310 (17,4), 450 (2,0)
		Ethanol	240 (11,4), 320 (9,7), 410 (12,5)
		Ethanol + EtONa	240 (14,8), 305 (3,14), 395 (20,5)
		Acetonitrile	245 (17,1), 320 (12,0), 440 (4,0), 550 (0,6)
		DMSO	440 (16,0)
$NC_6H_4OCH_3$-*p*	H	CCl_4	326 (17,2), 348 (16,9), 365 (17,0), 385 (10,3), 450 (3,1)
		Dioxane	308 (24,2), 360 (18,8), 460 (2,4), 520 (1,2)
		Ethanol	240 (11,5), 312 (8,4), 410 (12,1),
		Ethanol + EtONa	240 (15,1), 305 (3,6), 400 (21,5), 510 (1,2)
		Acetonitrile	244 (20,6), 320 (12,1), 440 (3,6), 550 (2,4)
		DMSO	418 (16,6), 455 (17,2)
2-Pyridylimino	H	Dioxane	300 (14,4), 400 (3,7)
		Ethanol	240 (8,1), 310 (4,6), 405 (10,7)
		Ethanol + EtONa	234 (11,6), 260 (8,1), 400 (14,5)
		Acetonitrile	234 (18,4), 295 (9,8), 420 (7,8)
		DMSO	295 (6,0), 430 (18,8)

TABLE 2. 3-Bromo-5-nitro-2-hydrocinnamaldehyde Imines (I, X = NR)

R	mp, °C	Found, %				Emperical formula	Calc., %			
		C	H	Br	N		C	H	Br	N
C_6H_5	158—160	51,8	3,0	22,9	8,0	$C_{15}H_{11}BrN_2O_3$	51,9	3,2	23,0	8,1
C_6H_4Me-*p*	219—220	53,1	3,5	22,0	7,2	$C_{16}H_{13}BrN_2O_3$	53,2	3,6	22,1	7,8
C_6H_4OMe-*p*	200—201	50,8	3,4	21,0	7,3	$C_{16}H_{13}BrN_2O_4$	50,9	3,4	21,2	7,4
2-Pyridyl	178—180	48,1	2,7	22,8	12,4	$C_{14}H_{10}BrN_3O_3$	48,3	2,9	23,0	12,1
C_6H_4Br-*p*	247—248	42,0	2,4	37,8	6,6	$C_{14}H_{10}Br_2N_2O_3$	42,0	2,3	37,8	6,6

It is apparent from Fig. 1 that a three-proton AMX system of signals of aldovinyl protons is present in the PMR spectrum of aldehyde I (X = 0) recorded in DMSO and in the PMR spectra of 2 hydroxycinnamaldehyde [3] and 5-nitro-2-hydroxycinnamaldehyde [1]: the doublet of the H_a aldehyde proton (the designations of the protons are given in formula Ia) is recorded at 9.61 ppm, with J_{ab} = 8 Hz, while the quartet centered at 6.94 ppm, with J_{bc} = 16 Hz, and the doublet at 7.90 ppm, with J_{cb} = 16 Hz, correspond to the signals of the H_b and H_c protons. The magnitude of the J_{bc} spin—spin coupling constant (16 Hz) indicates a trans configuration relative to the double bond. The absence in the strong-field part of the PMR spectrum of a signal of the proton in the 2 position in the 2-hydroxy-2H-chromene form I_c (X = 0) and a characteristic AB pattern of splitting of the protons of the CH=CH=OH group makes it possible to absolutely definitely exclude the Ic and Ib structures and to assign structure Ia, which is similar to the structure previously established for 2-hydroxy-5-nitrocinnamaldehyde [1], to 2-hydroxy-3-bromo-5-nitrocinnamaldehyde.

We obtained somewhat unexpected results during a study of the electronic absorption spectra of aldehyde I (X = 0) (Fig. 2 and Table 1), which were found to be extremely sensi-

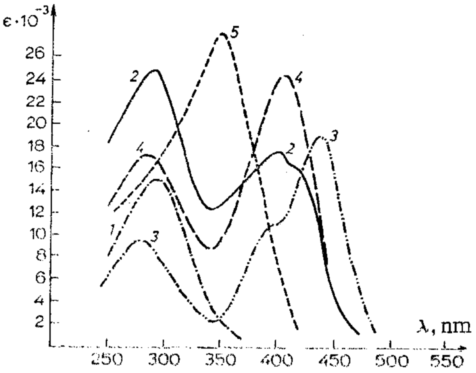


Fig. 2

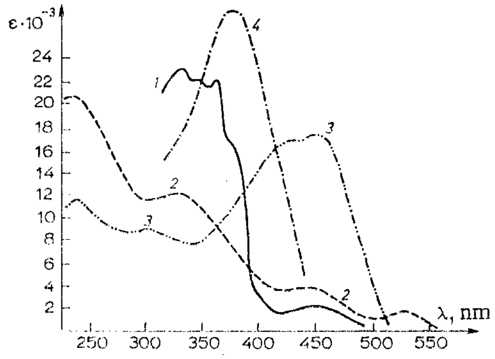


Fig. 3

Fig. 2. Electronic spectra of 3-bromo-5-nitro-2-hydroxycinnamaldehyde (I, X = 0): 1) in dioxane; 2) in ethanol; 3) in DMSO; 4) in ethanol in the presence of EtONa; 5) spectrum of 3-bromo-2-methoxy-5-nitrocinnamaldehyde.

Fig. 3. Electronic spectra of 3-bromo-5-nitro-2-hydroxycinnamaldehyde N-(p-methoxymethyl)imine: 1) in CCl_4; 2) in acetonitrile; 3) in DMSO; 4) spectrum of the O-methyl derivative of imine I (X = $NC_6H_4OCH_3$-p).

tive to a change in the polarity of the solvent at 400-450 nm. These spectra do not contain the band at 350 nm that is observed in the case of the O-methyl derivative — the analog of benzenoid form 1a. The absorption band that appears at 400-420 nm undergoes a pronounced increase in its intensity on passing to the proton-donor solvent ethanol and DMSO and coincides with the absorption band of the sodium salt of aldehyde I (X = 0). In the case of the spectrum of a solution in DMSO this band appears as a shoulder of a more intense absorption band at 450 nm.

The absorption band at 420 nm may be associated with the development of quanoid form Ib (X = 0). Since this form is not recorded by the PMR spectra in the case of more concentrated solutions, it must be assumed that the position of the tautomeric equilibrium for I (X = 0) has a marked concentration dependence. This sort of concentration dependence is quite well known for prototropic tautomerism [4].

As a consequence of the greater basicity of the nitrogen atom as compared with the oxygen atom, the stability of structure Ib should increase on passing from aldehyde I (X = 0) to imines I (X = NR). In the general case the formation of the protonated $-CH=\overset{+}{N}HR$ group significantly increases the electrophilicity of the carbon atom bonded to this group [5], which, according to [6], should promote the formation of ring structure Ic.

The information noted above is in complete agreement with the results of a study of the vibrational, electronic, and PMR spectra of a series of 3-bromo-5-nitro-2-hydrocinnamdehyde imines I (X = NR), the principal characteristics of which are presented in Tables 1 and 2. Their IR spectra (mineral oil) contain ν_{NH} bands at 3325 cm^{-1} and $\nu_{C=C}$ bands in the region characteristic for the 2H-chromene structure (1650-1660 cm^{-1}).

It is apparent from Fig. 3, in which the typical electronic absorption spectrum of imine (X = $NC_6H_4OCH_3$-p) is presented, that the spectrum does not contain the band of benzenoid form Ia that is observed for the O-methyl derivative at 370 nm; however, a broad structured band at 300-350 nm, the presence of which is usually associated with the existence of the cyclic 2H-chromene structure [1], appears in the spectrum of a solution in CCl_4.

An examination of the PMR spectrum of 3-bromo-5-nitro-2-hydroxycinnamaldehyde N-phenylimine (Fig. 4) recorded in acetonitrile gives additional evidence for the cyclic structure of imines I (X = NR). It is apparent from Fig. 4b that the spectrum of imine I (X = NPh) does not contain the signal of the H_a proton that appears in the spectrum of aldehyde I (X = 0) in the weak-field region. At the same time, the spectrum does contain a multiplet at 6.40 ppm and a quartet at 6.16 ppm of the H_a' and H_b' protons (the designations of the protons are given in formula Ic), which correspond to the AB part of a complete ABMX system of proton signals that is characteristic for 2H-chromene structures [1]. The H_c' signal is found in the aromatic-proton region, whereas the signal of the proton of the X = NH group is recorded at

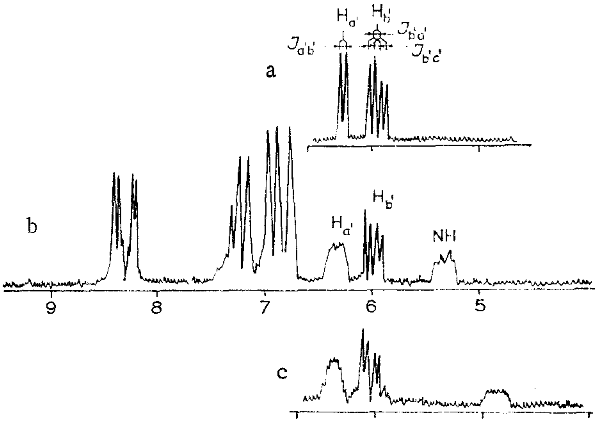


Fig. 4. PMR spectrum of 3-bromo-5-nitro-2-hydroxycinnamaldehyde N-phenylimine (I, X = C_6H_5): a) in acetonitrile after deuteration; b) in acetonitrile; c) spectrum of the ^{15}N-phenylimine.

5.48 ppm. After deuteration (Fig. 4a), the multiplet of the $H_{a'}$ proton is simplified to a doublet. Isotopic replacement by ^{15}N in the PMR spectrum of I (X = ^{15}NPh) (Fig. 4c) gives rise to the splitting of the signal that is characteristic for the ^{15}N—H group [1].

EXPERIMENTAL

The electronic absorption spectra of solutions of the compounds (c = 10^{-4}–10^{-5} mole/liter) were recorded with a Specord UV-vis spectrophotometer. The IR spectra of mineral oil suspensions were obtained with a UR-20 spectrometer. The PMR spectra of solutions (10-15%) of the compounds were measured with a Varian XL-100/15 radiospectrometer (100 MHz).

3-Bromo-5-nitro-2-hydroxycinnamaldehyde (I, X = O). This compound was prepared by the method in [2] by condensation of 3-bromo-5-nitrosalicylaldehyde and acetaldehyde in an alkaline medium. Workup gave yellow needles, with mp 194°C (from toluene), in 65% yield. Found: C 40.2; H 2.6; Br 28.9%. $C_9H_6BrNO_4$. Calculated: C 39.7; H 2.2; Br 29.4%.

3-Bromo-2-methoxy-5-nitrobenzaldehyde. A 7 g sample of silver oxide was added to a solution of 9.8 g (0.04 mole) of methyl iodide, and the mixture was refluxed for 3 h. The precipitate was removed by filtration, and the filtrate was evaporated to give a yellow powder with mp 100°C (from ethanol). Found: C 36.9; H 2.3; Br 30.6%. $C_8H_6BrNO_4$. Calculated: C 36.9; H 2.3; Br 30.7%.

3-Bromo-2-methoxy-5-nitrocinnamaldehyde. A 1.7 g (0.04 mole) sample of acetaldehyde was added with stirring to a cooled (−12°C) suspension of 5.2 g (0.02 mole) of 3-bromo-2-methoxy-5-nitrobenzaldehyde in 70 ml of ethanol, and a 10% aqueous solution of sodium hydroxide was added slowly dropwise until the mixture had pH 8-9 and the dispersed phase had dissolved. The reaction mixture was then stirred at no higher than 0-5°C for 4 h. The precipitated aldehyde was removed by filtration and washed with acidified water to give bright-yellow crystals, with mp 173°C (from ethanol), in 75% yield. PMR sepctrum (CCl_4): 3.95 ppm (3H, s, OCH_3). Found: C 41.9; H 2.7; Br 27.8%. $C_{10}H_8BrNO_4$. Calculated: C 42.0; H 2.8; Br 28.0%.

3-Bromo-5-nitro-2-hydroxycinnamaldehyde Imines (I, X = NR). These compounds were obtained by mixing alcohol solutions of equimolar amounts of aldehyde I (X = O) and the corresponding amines. The characteristics of the imines are presented in Table 2.

3-Bromo-2-metoxy-5-nitrocinnamaldehyde N-Phenylimide. This compound was prepared from 2-methoxy-3-bromo-5-nitrocinnamaldehyde and aniline in ethanol. Workup gave yellow crystals with mp 127°C (from ethanol). Found: C 53.1; H 3.5; Br 22.0; N 7.5%. $C_{15}H_{13}BrNO_3$. Calculated: C 53.2; H 3.6; Br 22.1; N 7.8%.

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SYNTHESIS AND STUDY OF THE LIGHT-STABILIZING ACTIVITY OF SOME DITHIOCARBAMATES THAT INCLUDE A HETEROAROMATIC RING

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A number of new dithiocarbamates of transition metals that contain thiophene, furan, benzo[b]thiophene, and benzo[b]selenophene rings were synthesized. The compounds obtained were investigated as light stabilizers for polymers. It is shown that the effectiveness of the light-stabilizing effect of the dithiocarbamate depends on the structure of the heterocyclic fragment included in its composition.

At the end of the nineteen fifties in the laboratory of heterocyclic compounds of the Institute of Organic Chemistry of the Academy of Sciences of the USSR a number of thiophene derivatives were synthesized in order to search for new vulcanization accelerators and antioxidants for rubbers [1, 2]. During testing of these compounds it was established that some of them have the properties of inhibitors of the oxidation of rubbers, although to a smaller degree than the compounds that do not include a thiophene ring that are used for this purpose. Later one of the authors of the present paper in collaboration with B. P. Fedorov and G. I. Gorushkina [3] synthesized some dithiocarbamates that include a thiophene ring, the properties of which, however, were not investigated. It has been recently established that the dithiocarbamates of some transition metals are effective light and heat stabilizers of polymers [4]. In this case it should be noted that the nature of the transition metal plays a substantial role in the effectiveness of the dithiocarbamates. In connection with all of the information pointed out above we again turned to the synthesis of dithiocarbamates of the type mentioned above by extending the number of transition metals. The resulting dithiocarbamates were studied as light stabilizers. The results of the study are set forth below.

The new dithiocarbamates were synthesized by known methods. The reaction of 2-formylthiophene (I) and substituted 2-formylthiophenes (II), as well as furfural (V) and 2-formylbenzo[b]thiophene (III) or 2-formylbenzo[b]selenophene (IV), with the corresponding amines (VI-VIII) gave azomethines IX-XV, which were reduced to amines XVI-XXII. The latter were converted to alkali metal or ammonium salts of N,N-disubstituted dithiocarbamic acids, from which dithiocarbamates XXIII-XXXV were obtained by exchange reactions with transition metal salts. The properties of the dithiocarbamates obtained are presented in Table 1. Let us note that the synthesis of dithiocarbamate complexes XXX and XXIX was accompanied by the formation of a compound with an unestablished structure, the decomposition of which in an acidic medium led to the formation of XXX.*

Complexes XXXIV and XXXV were obtained from the crystalline ammonium salts of the dithiocarbamic acids with a benzo[b]thiophene or benzo[b]selenophene fragment in the molecules. These salts are convenient to use directly for the preparation of complexes XXXIV and XXXV.

Using ethyl- and methoxythiophene as the ligand for the preparation of nickel complex XXXIII we strove, as in the introduction of a tert-butyl group as the substituent attached to the nitrogen atom in XXIII, to increase the solubility [5] and the effectiveness of the

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*As in Russian original — Publisher.

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