1a-Bromo-5,5-dioxo-2-(N,N-dimethylimino)thiolano[3,4-d]-1,3-dithiolane Bromide (IIa). A 0.54-ml (0.01 mole) portion of bromine is added dropwise, slowly and with stirring, to a suspension of 2.37 g (0.01 mole) of 1,1-dioxo-3-thiolen-3-yl ester of N,N-dimethyldithiocarbamic acid Ia in 90 ml of $CHCl_3$. The orange precipitate is filtered, transferred into a beaker, soaked with 3-5 ml of acetone, and ground with a glass rod until a white powder is obtained. The precipitate is filtered, washed with acetone, and dried. Yield 2.1 g (52%), mp 196-198°C (from acetic acid). Found, %: Br 40.6; N 3.8; S 23.9. $C_7H_{11}Br_2NO_2S_3$. Calculated, %: Br 40.3; N 3.5; S 24.2.

When the reaction was carried out in acetic acid, compound IIa was obtained in a yield of 2.4 g (59%).

1a-Bromo-5,5-dioxo-2-(N,N-diethylimino)thiolano[3,4-d]-1,3-dithiolane Bromide (IIb). A 0.54-ml (0.01 mole) portion of bromine is added dropwise, slowly and with stirring, to a solution of 2.65 g (0.01 mole) of 1,1-dioxo-3-thiolen-3-yl ester of N,N-diethyldithiocarbamic acid Ib in 15 ml of $CHCl_3$. The precipitate is treated as described above. Yield 3.5 g (83%), mp 201-202°C (from acetic acid). Found, %: Br 37.4; N 3.4; S 22.2. $C_9H_{15}Br_2NO_2S_3$. Calculated, %: Br 37.7; N 3.3; S 22.6.

Preparation of Perchlorates IIIa, b. A solution of 0.02 mole of $NaClO_4$ in 5 ml of H_2O is added to a saturated solution of 0.01 mole of bromides IIa, b in water. The precipitate is filtered, washed with water, and dried in air.

LITERATURE CITED

1. K. Hirtani, H. Shiano, and M. Okawara, Chem. Lett., 867 (1973).
2. Y. Ueno, A. Nakayama, and M. Okawara, Synthesis, No. 4, 277 (1975).
3. T. É. Bezmenova, G. I. Khaskin, V. I. Slutskii, P. G. Dul'nev, L. N. Zakharov, V. I. Kulishov, and Yu. T. Struchkov, Khim. Geterotsikl. Soedin., No. 7, 907 (1981).
4. T. Nakai and M. Okawara, Bull. Chem. Soc. Jpn., No. 6, 1864 (1970).

COMPARATIVE STUDY OF RING-CHAIN ISOMERIC TRANSITIONS OF 2-CYANO-SUBSTITUTED BENZAMIDES AND BENZENESULFAMIDES*

R. É. Valter, R. B. Kampare, S. P. Valtere, D. É. Balode, and A. É. Batse

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The rate constants of cyclization and the constant of ring-chain equilibrium of N-isopropyl-2-cyano-substituted benzamide and benzamide and benzenesulfamide by the methods of PMR and IR spectroscopy, and it was shown that in the transition from 2-cyanobenzamides to 2-cyanobenzenesulfamides a sharp destabilization of the cyclic isomeric form is observed; however, the cyclization of 2-cyanobenzenesulfamides proceeds at a higher rate than the cyclization of 2-cyanobenzamides.

N-Monosubstituted-2-cyanobenzamides (I) and their ring isomers — 3-iminoisoindolines (II) — are not interconverted in dioxane at room temperature [2]. N-Monosubstituted-2-cyanobenzenesulfamide (III) and 3-iminobenzisothiazoline-1,1-dioxides (IV) behave analogously in dioxane; however, the equilibrium III $\rightleftarrows$ IV was detected in a solution of dioxane +10% triethylamine, where the ring-chain equilibrium constants were measured by the method of IR spectroscopy.

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Riga Polytechnic Institute, Riga 226355.

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TABLE 1. Rate Constants of Isomeric Conversions and Ring-Chain Equilibrium of N-Isopropyl-2-cyanobenzamide and N-Isopropyl-2-cyanobenzenesulfamide (in CD_3OD at 25°C)

Conversion	Signals of the protons of the methyl groups of $CH(CH_3)_2$, doublets, δ, ppm		$k_1 \cdot 10^4$, sec^{-1}	$k_2 \cdot 10^4$, sec^{-1}	K
	open isomer	cyclic isomer			
Id→IId	1,21	1,49	0,58	—	>50
IIId⇄IVd	1,02	1,53	4,5[a]	10,1[a]	0,45
			4,2[b]	9,2[b]	0,46

[a]When equilibrium was reached starting with the open isomer.
[b]The same, starting with the cyclic isomer.

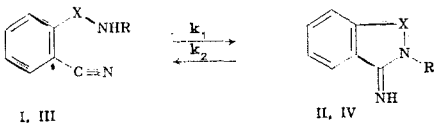
TABLE 2. The Most Important Bands (cm^{-1}) in the IR Spectra of 2-Cyanobenzamides Ia-e and 3-Iminoisoindolinones IIa-e (in dioxane + 10% triethylamide)

Compound	I		II	
	amide I	amide II	νC=O	νC=N
a	1694	1623	1742	1674
b	1672	1537	1733	1652
c	1668	1536	1736	1656
d	1666	1536	1729	1646
e	1687	1541	1752, 1736	1665
e[a]	1676	—	1750, 1734	1657

[a]In principle, the amide II band is masked by the absorption of the solvent.

Among the N-monosubstituted 2-cyanobenzamides, the isomerization cyclization was studied in detail only for 2-cyanobenzanilide (Ie) [3] and its derivatives possessing substituents in the N-phenyl group [4]; moreover, it has been established [3] that the equilibrium Ie ⇄ IIe, strongly shifted to the right, is observed in polar aprotic solvents (DMSO, N-methylpyrrolidone, dimethylacetamide, HMPA). It has also been established [3] that the addition of bases to solutions greatly accelerates the cyclization Ie → IIe.

The purpose of this work was a comparative study of the ring-chain isomeric conversions of N-monosubstituted 2-cyanobenzamides (I ⇄ II) and 2-cyanobenzenesulfamides (III ⇄ IV).



I, III II, IV

I, II X=CO; III, IV X=SO_2; I—IV a R=H; b R=C_2H_5; c R=C_3H_7; d R=*i*-C_3H_7; e R=C_6H_5

It was shown by the method of IR spectroscopy that, in contrast to N-alkyl-2-cyanobenzenesulfamides [1], N-unsubstituted and N-alkyl-2-cyanobenzamides (Ia-d) and 3-iminoisoindolinones (IIa-d) proved stable in a solution of dioxane + 10% triethylamine, and the equilibrium I ⇄ II could not be observed. Only for 2-cyanobenzanilide (Ie) in this solution, as well as in pyridine, was a complete shift of the equilibrium (within the limits of sensitivity of the method of IR spectroscopy) observed in the direction of the cyclic isomer IIe, which agrees with the data of [3]. The rate constants of the isomerization Ie → IIe were measured by the method of IR spectroscopy: $k_1 = 9 \cdot 10^{-3} \pm 0.8 \cdot 10^{-3}$ sec^{-1} (in dioxane + 10% triethylamine at 20°C) and $8 \cdot 10^{-3} \pm 1 \cdot 10^{-3}$ sec^{-1} (in pyridine). Let us note that for 2-cyanobenzenesulfanilide under the same conditions, the ring-chain equilibrium

IIIe ⇄ IVe, shifted in the direction of the open isomer (K = 0.15 ± 0.02 in a solution of dioxane + 10% triethylamine at 20°C) was detected [1].

The behavior of open (Id, IIId) and cyclic (IId, IVd) isomers of N-isopropyl derivatives in CD_3OD solution was investigated by the PMR method. Quantitative measurements were performed according to the intensities of the signals of the CH_3 protons of the isopropyl groups. It was established that for N-isopropyl-2-cyanobenzamide (Id), the ring-chain equilibrium is entirely shifted in the direction of the cyclic isomer (within the limits of sensitivity of the PMR method) within 24 h, while for N-isopropyl-2-cyanobenzenesulfamide a ring-chain equilibrium IIId → IVd is observed (K = 0.45 in CD_3OD at 25°C). However, in this case it is important to note that the rate constant (k_1) of the cyclization Id → IId is almost an order of magnitude lower in comparison with the cyclization IIId → IVd (Table 1).

Thus, in the transition from 2-cyanobenzamides I to 2-cyanobenzenesulfamides III, a sharp destabilization of the cyclic isomeric form is observed, which can be explained [5] by the lower nucleophilicity of the nitrogen atom of the sulfamide group in comparison with the carboxamide group. However, the rate-limiting step of cyclization evidently is the stripping of a proton (see [3, 4, 6]), and sulfamides possessing a substantially greater NH acidity have a lower activation energy for the cyclization reaction in comparison with carboxamides.

Evidently, the fact that both isomers Ie and IIe can be isolated in individual form for 2-cyanobenzanilide [2], while only the cyclic isomer IVe can be isolated individually for 2-cyanobenzenesulfamide [1] is not a confirmation of greater thermodynamic stability of the open isomer Ie in comparison with IIIe, but is due only to a larger activation energy for the transition I → II in comparison with the cyclization III → IV.

EXPERIMENTAL

The IR spectra were recorded on an IKS-14A instrument for solutions in dioxane + 10% triethylamine and in pyridine. The concentration of the solution was $2.5 \cdot 10^{-2}$ M, layer thickness 0.011 cm. The frequencies of the most important bands in the IR spectra of compounds Ia-e and IIa-e are cited in Table 2. The rate constant of cyclization Ie → IIe was determined according to the change in the intensity of the amide I (form I) and νC=O (form II) bands.

The PMR spectra were recorded on a Tesla BS 487C instrument in a solution of CD_3OD at 25°C (without internal standard), concentration of the solutions $5 \cdot 10^{-2}$ M. The equilibrium constants and the rates of isomerization were calculated according to the changes in the signal intensities of the CH_3 protons of the isopropyl groups in both isomers (see Table 1). The equilibrium IIId ⇄ IVd was reached on the basis both of the open (IIId) and of the cyclic (IVd) isomers.

Compounds Ia-e, IIa-e, IIId, and IVd were produced by the methods of [1, 2].

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LITERATURE CITED

1. D. É. Balode, R. É. Valter, and S. P. Valter, Khim. Geterotsikl. Soedin., No. 2, 1632 (1978).
2. R. É. Valter, A. É. Batse, and S. P. Valter, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 6, 726 (1972).
3. S. G. Tadevosyan, É. N. Teleshov, I. V. Vasil'eva, and A. N. Pravednikov, Zh. Org. Khim., 16, 353 (1980).
4. I. V. Vasil'eva, S. G. Tadevosyan, É. N. Teleshov, and A. N. Pravednikov, Dokl. Akad. Nauk SSSR, 256, 398 (1981).
5. R. É. Valter, Usp. Khim., 51, 1374 (1982).
6. L. Yu. Yusefovich, B. M. Sheiman, V. G. Mairanovskii, and T. M. Filippova, Khim. Geterotsikl. Soedin., No. 5, 616 (1979).