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COMPARATIVE STUDY OF THE STRUCTURE OF RHODANINE, ISORHODANINE, THIAZOLIDINE-2,4-DIONE, AND THIORHODANINE

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Ab initio (HF and MP2 level) and semiempirical (AM1, PM3, MNDO) calculations on the relative stabilities and structures of the potential tautomeric forms of rhodanine, isorhodanine, thiazolidine-2,4-dione, and thiorhodanine are reported. Ab initio calculations predict that the thiooxo, oxothio, dioxo, and dithio tautomers are the most stable. These results correspond to the known experimental data. Infrared spectra of the investigated compounds were recorded for the region 4000-150 cm^{-1}, and the characteristic bands were compared with ab initio calculated frequencies at the HF/3-21G(*) level.*

Keywords: *ab initio* calculations, IR spectra, structure, tautomerism.

Thiazolidin-4-one-2-thione (rhodanine **1**), thiazolidin-2-one-4-thione (isorhodanine **2**), thiazolidine-2,4-dithione (thiorhodanine **4**), and thiazolidine-2,4-dione (**3**) as well as some of their derivatives are of industrial importance. The rhodanines find application as vulcanizing agent for different kinds of rubber. Isorhodanine, thiorhodanine, and thiazolidine-2,4-dione have a weaker influence on vulcanizing rate [1]. Addition of rhodanine, thiazolidine-2,4-dione, and some of their derivatives to photosensitizing compositions leads to improvement of the qualities of these compositions [2, 3]. Different thiazolidine-2,4-dione derivatives have antimiotic [4], hypoglycemic [5], hypocholesterolemic [5], anti-inflammatory [6], antihyperlipemic [7], and anti-diabetic [8] action. Thiazolidine-2,4-dione is an inhibitor of the corrosion of mild steels in acidic solution. A possible explanation of its ability to inhibit metallic corrosion is its coordination at the metallic surface. Rhodanine, thiorhodanine, and their azo derivatives are suitable as ligands in coordination compounds [9]. These compounds are also used in analytical chemistry as highly sensitive reagents for heavy metals [10, 11].

Compounds **1-4** may exist theoretically in five tautomeric forms as shown in Fig. 1. Their tautomerism was studied experimentally by different authors (see the citations in. [12]). The structures of rhodanine [13] and thiazolidine-2,4-dione [14] determined by X-ray studies have been reported. Experimental (UV-vis spectroscopy) as well as theoretical quantum-chemical investigations of the electronic structure and tautomeric equilibrium of rhodanine, isorhodanine, thiazolidine-2,4-dione, and thiorhodanine were reported by Hilal et al. [15]. However, semiempirical quantum-chemical calculations in this work have been performed in the π-electron approximation by means of the Pariser–Parr–Pople method. Photoelectron spectroscopy and CNDO/2 theoretical investigations of the tautomers **A** of rhodanine and thiazolidine-2,4-dione (Fig. 1) were carried out in [16]. Detailed tautomeric study of rhodanine, isorhodanine, and thiazolidine-2,4-dione has been carried out by IR, ^{1}H and ^{13}C NMR, and mass spectrometry [17]. It has been found that these compounds exist in thiooxo, oxothio, and dioxo tautomeric forms. We have reported [18] *ab initio* and semiempirical (MNDO, AM1, MNDO-PM3) investigations on the tautomerism of rhodanine.

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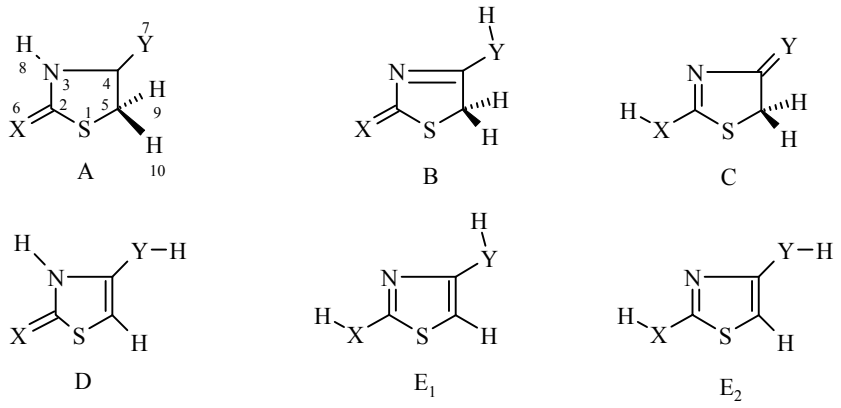

Fig. 1. Tautomeric forms of rhodanine (X = S, Y = O) **1**, isorhodanine (X = O, Y = S) **2**, thiazolidine-2,4-dione (X = O, Y = O) **3**, and thiorhodanine (X = S, Y = S) **4**.

The aim of the present study was to compare the relative stabilities of tautomers of rhodanine, isorhodanine, thiorhodanine, and thiazoline-2,4-dione as well as the structures and IR spectra of the most stable tautomers. The quantum-chemical calculations were done using *ab initio* and semiempirical methods. In this work we present theoretical and experimental investigation on the IR spectra of the above-mentioned compounds with *ab initio* methods.

In order to estimate the reliability of the methods used for predicting the properties of sulfur-containing compounds, the relative stabilities of different tautomeric forms, the geometric and electronic aspects, and the IR spectra of the most stable tautomers were studied. The bond lengths and bond angles were considered as geometric description of the molecules while the dipole moments were used for description of the electronic distribution.

In agreement with the experiment [12, 17] *ab initio* calculations show that tautomer **A** is the most stable for all compounds studied (Table 1). The difference between relative stabilities of tautomer **A** and the next low-lying tautomer is more than 10 kcal/mol. The relative stabilities of **A** and **B**, **C** and **D** tautomeric forms were evaluated from calculations at the MP2(fc)/6-31G**//HF/3-21G$^{(*)}$* and HF/6-31G**//HF/3-21G$^{(*)}$* levels. Those obtained from the latter turn out to be higher by 0.1-0.9 kcal/mol. Only for rotamers of tautomer **E** is the difference in the range 2.5-4.0 kcal/mol. Semiempirical AM1, MNDO-PM3, and MNDO calculations do not agree even qualitatively, neither with the experimental data [12] nor with the *ab initio* results for compounds with exocyclic sulfur (rhodanine, isorhodanine, and thiorhodanine). An exception is the AM1 calculation for rhodanine where only a qualitative agreement between experiment and quantum-chemical calculations (*ab initio* and semiempirical) for thiazolidine-2,4-dione exists.

Structural data for rhodanine [13] and thiazolidine-2,4-dione [14] in the solid state are available. However, there are no published experimental data on the structures of isorhodanine and thiorhodanine. The HF/3-21G$^{(*)}$* and HF/6-31G** optimized structural parameters of the most stable tautomers **A** for the above-mentioned investigated compounds with the available X-ray data are given in Table 2. Geometry optimization of tautomer **A** for rhodanine and thiazolidine-2,4-dione at the HF/3-21G$^{(*)}$* level led to a minimum energy structure that is close in bond lengths and angles to the geometry found in the crystal as well as to those obtained at the HF/6-31G** level. For example, the differences in the C–S and C=S bond lengths calculated with 6-31G** and 3-21G$^{(*)}$* basis sets do not exceed 0.003 and 0.006 Å respectively. The difference is substantial for the carbon–carbon bond lengths where calculations with the 6-31G** basis set predict shorter (0.011-0.016 Å) distances in comparison with the experiment.

TABLE 1. Calculated Relative Stabilities (kcal/mol) of the Tautomers **A-E** (Fig. 1) of Rhodanine, Isorhodanine, Thiazolidine-2,4-dione, and Thiorhodanine at Different Computational Levels

Computational level	Tautomers						Tautomers					
	A	**B**	**C**	**D**	**E_1**	**E_2**	**A**	**B**	**C**	**D**	**E_1**	**E_2**
	Rhodanine **1**						Thiazolidine-2,4-dione **4**					
MNDO	0.57	6.47	2.73	9.32	0.00	2.76	0.00	7.45	8.45	9.36	7.21	10.02
PM3	3.83	18.91	0.00	11.22	2.02	3.48	0.00	14.07	16.42	10.04	20.07	21.66
AM1	0.00	16.22	8.52	10.90	7.68	10.77	0.00	18.47	19.34	12.73	20.23	23.31
HF/DH//HF/DH	0.00	22.59	32.36	18.23	38.45	42.85	0.00	20.78	25.05	21.18	33.92	38.07
HF/3-21G$^{(*)*}$//HF/3-21G$^{(*)*}$	0.00	21.51	28.97	9.99	26.68	30.05	0.00	18.79	20.68	13.31	21.62	24.70
HF/4-31G**//HF/4-31G**	0.00	17.71	14.19	22.45	23.96	27.05	0.00	15.66	18.66	25.35	32.02	34.75
HF/6-31G**//HF/3-21G$^{(*)*}$	0.00	17.58	16.40	21.59	26.00	29.03	0.00	15.36	18.69	25.37	32.00	34.69
MP2(fc)/6-31G**//HF/3-21G$^{(*)*}$	0.00	16.84	15.83	20.92	22.07	25.08	0.00	15.44	18.86	24.25	29.49	32.00
	Isorhodanine 2						Thiorhodanine **4**					
MNDO	2.06	3.48	8.68	2.93	0.00	2.03	10.20	9.79	10.38	10.24	0.00	1.99
PM3	11.22	5.95	28.44	0.00	8.31	10.65	25.34	20.73	22.28	10.91	0.00	2.21
AM1	0.20	6.56	17.34	0.00	5.31	7.80	7.50	11.53	13.72	5.39	0.00	2.51
HF/DH//HF/DH	0.00	30.06	26.15	25.01	37.32	38.72	0.00	31.50	33.37	21.93	41.54	43.09
HF/3-21G$^{(*)*}$//HF/3-21G$^{(*)*}$	0.00	26.27	22.61	14.78	22.90	23.54	0.00	28.53	30.63	11.26	27.58	28.43
HF/4-31G**//HF/4-31G**	0.00	11.77	20.03	14.23	21.65	22.05	0.00	13.65	15.54	11.46	13.65	14.24
HF/6-31G**//HF/3-21G$^{(*)*}$	0.00	14.11	20.10	16.36	23.62	23.91	0.00	16.00	17.70	12.49	17.33	17.79
MP2(fc)/6-31G**//HF/3-21G$^{(*)*}$	0.00	13.90	19.73	15.56	21.58	21.87	0.00	15.34	16.80	12.83	14.74	15.28

TABLE 2. *Ab initio* calculated (3-21G$^{(*)}$* and 6-31G** basis sets) structure parameters for tautomer A of thiazolidin-2,4-one and thiorhodanine. Bond lengths are in Å and bond angles in degrees. For numbering of the atoms see Fig. 1

Bond	*d*, Å			Bond angle	ω, deg		
	exptl.[a]	3-21G$^{(*)}$*	6-31G**		exptl.[a]	3-21G$^{(*)}$*	6-31G**
1	2	3	4	5	6	7	8
			Rhodanine **1**				
C5-S1	1.82	1.814	1.814	C5-S1-C2	92.7	93.1	93.1
S1-C2	1.74	1.756	1.756	S1-C2-N3	118.8	110.2	109.9
C2-N3	1.37	1.364	1.356	C2-N3-C4	116.8	119.9	119.9
N3-C4	1.38	1.386	1.380	N3-C4-C5	112.3	109.7	110.3
C5-C4	1.51	1.527	1.516	C4-C5-S1	106.3	107.2	106.8
C4-O7	1.23	1.201	1.184	N3-C4-O7	123.3	124.3	124.1
C2-S6	1.64	1.627	1.630	N3-C2-S6	124.8	125.7	125.4
N3-H8		0.992	0.998	H8-N3-C4		120.3	120.2
C5-H9(H10)		1.078	1.081				
			Isorhodanine **2**				
C5-S1		1.819	1.818	C5-S1-C2		92.4	92.0
S1-C2		1.770	1.771	S1-C2-N3		109.4	109.4
C2-N3		1.396	1.388	C2-N3-C4		120.2	120.2
N3-C4		1.352	1.345	N3-C4-C5		110.2	110.5
C5-C4		1.530	1.515	C4-C5-S1		107.2	107.9
C4-S7		1.625	1.631	N3-C4-S7		125.9	125.3
C2-O6		1.198	1.179	N3-C2-O6		124.4	124.2
N3-H8		0.992	0.998	H8-N3-C4		120.9	121.1
C5-H9(H10)		1.077	1.080				

TABLE 2 (continued)

1	2	3	4	5	6	7	8
			Thiazolidin-2,4-one **3**				
C5-S1	1.845	1.812	1.815	C5-S1-C2	94.2	92.7	92.5
S1-C2	1.751	1.777	1.779	S1-C2-N3	111.2	109.6	109.6
C2-N3	1.372	1.381	1.375	C2-N3-C4	117.5	119.8	119.6
N3-C4	1.373	1.375	1.372	N3-C4-C5	113.6	110.1	110.7
C5-C4	1.547	1.529	1.519	C4-C5-S1	103.6	107.8	107.5
C4-O7	1.219	1.203	1.185	N3-C4-O7	122.7	124.9	124.6
C2-O6	1.209	1.200	1.183	N3-C4-O6	123.9	125.5	125.2
N3-H8	0.900	0.991	0.996	H8-N3-C4	130.0	120.6	120.9
C5-H9(H10)		1.078	1.080	C2-N3-H8	112.0	119.6	119.5
				S1-C2-O6	124.9	124.9	125.1
				O6-C2-N3	123.9	125.9	125.2
				O7-C4-C5	123.7	125.0	124.6
			Thiorhodanine **4**				
C5-S1		1.823	1.818	C5-S1-C2		92.8	92.6
S1-C2		1.750	1.748	S1-C2-N3		109.8	109.5
C2-N3		1.378	1.367	C2-N3-C4		120.4	120.6
N3-C4		1.362	1.353	N3-C4-C5		109.8	110.2
C5-C4		1.527	1.511	C4-C5-S1		107.1	107.1
C4-S7		1.622	1.628	N3-C4-S7		125.4	124.8
C2-S6		1.623	1.626	N3-C4-S6		124.8	124.6
N3-H8		0.993	0.999	H8-N3-C4		120.4	120.3
C5-H9(H10)		1.077	1.081	C2-N3-H8		119.2	119.1
				S1-C2-S6		125.4	125.9
				S6-C2-N3		124.8	124.6
				S7-C4-C5		124.8	125.0

[a] Rhodanine **1** taken from [13]; thiazolidin-2,4-one **3** from [13].

TABLE 3. Calculated Dipole Moments (in Debyes) and Ionization Potentials (in eV) for Tautomers A of Compounds **1-4** (Fig. 1)

Com-pound	Computational level						exptl.
	MNDO	AM1	PM3	3-21G(*)*	4-31G**	6-31G**	
				Dipole moment			
1A	1.84	1.85	2.63	2.79	2.16	2.73	2.20 [41]
2A	1.42	1.56	1.12	1.72	1.75	1.65	
3A	1.78	1.88	1.61	1.95	1.87	1.86	2.03 [41]
4A	3.20	1.50	1.48	2.19	1.97	2.28	
				Ionization potential			
1A	9.65	9.25	9.47	9.68	9.34	9.60	9.26 [16]
2A	9.78	9.33	9.56	9.65	9.42	9.68	
3A	10.84	9.99	10.19	10.74	10.64	10.77	10.14 [16]
4A	9.46	9.14	9.59	9.51	9.26	9.61	

The results for dipole moments and ionization potentials calculated at different computational levels are given in Table 3. It can be seen that available experimental values for dipole moments and ionization potentials of rhodanine **1A** and thiazolidine-2,4-dione **3A** are in general in good agreement with the calculated HF/4-31G** ones. Excellent agreement was also found for the measured ionization potentials of **1A** and **3A** and the respective AM1 and PM3 calculated values (Table 3).

The vibrational spectra of the most stable tautomers **A** for the compounds studied were computed using 3-21G$^{(*)}$* *ab initio* basis set. Experimental data of the vibrational frequencies of **A** measured in CsI and $CHCl_3$ are also presented for comparison. All results are given in Table 4. Our assignments for the *ab initio* calculated frequencies are based upon the analysis of the corresponding vibrational eigenvectors. Interpretation of the calculated IR spectra is not easy since most of the normal modes are not characteristic. Only a few modes, such as the NH, CH, C=O stretching and CH_2 deformation, were found to be isolated.

Comparing the calculated spectra of the compounds with the exocyclic sulfur atom and the spectrum of their dioxo analogue, thiazolidine-2,4-dione, we found that the wavenumbers of the NH stretching vibrations are lower when oxygen is replaced by the sulfur atom. The NH stretching vibrations are calculated to be at 3482, 3476, and 3470 cm^{-1} in the spectra of rhodanine, isorhodanine, and thiorhodanine, respectively. In the thiazolidine-2,4-dione the corresponding band was calculated at 3492 cm^{-1}. The same tendency was observed experimentally (Table 4).

A very intense carbonyl stretching band at 1730 cm^{-1} was observed in a $CHCl_3$ solution of isorhodanine. This band is shifted up to 1744 cm^{-1} in the solid state spectrum. The carbonyl stretching band of rhodanine in the $CHCl_3$ solution appears as a doublet (1723, 1759 cm^{-1}) arising probably from resonance phenomena. The existence of hydrogen bond dimers in the solutions used for measurements is improbable since their low concentration of about 0.5% can hardly lead to formation of hydrogen bonding. The low solubility of rhodanine in this solvent does not permit one to determine the position of the carbonyl band or the behavior of the NH stretchings. The C=O band is strongly shifted down to 1711 cm^{-1} in the solid state spectrum due to the strong intermolecular hydrogen bonding. Therefore, the mean value of 1741 cm^{-1} obtained from the positions of both maxima (1723 and 1759 cm^{-1}) was taken for comparison with the calculations. A similar situation is observed for the symmetric CH_2 stretching band where the mean value 2891 cm^{-1} of the doublet frequencies 2915 and 2867 cm^{-1} from the CsI spectrum was used for the same purpose. Both carbonyl bands observed in thiazolidine-2,4-dione at 1755 and 1704 cm^{-1} in chloroform solution and 1738 and 1659 cm^{-1} in the solid state (CsI pellet) respectively are easily assigned from the theoretical values 1756 and 1711 cm^{-1} and their eigenvectors. The corresponding calculated intensities 176 and 738 km/mol also confirm the experimental picture.

TABLE 4. HF/3-21G(*)* Calculated and Experimental IR Data for Tautomer A of Compounds **1-4**. (Frequencies (ν) are in cm^{-1} and Intensities (*I*) in km/mol)

Calculated		Experimental		Assignment	Calculated		Experimental		Assignment
ν	*I*	$CHCl_3$	CsI		ν	*I*	$CHCl_3$	CsI	
1	2	3	4	5	6	7	8	9	10
		Rhodanine **1**					Isorhodanine **2**		
3482	114	3379 m	3091 m	NH str.	3476	115	3374 m	3173 m	NH str.
3006	1	*	2960 m	CH_2 as. str.	3018	3	*	2950 w	CH_2 as. str.
2948	5	*	2891 m	CH_2 sym. str.	2958	8	*	2920 m	CH_2 sym. str.
1750	444	1741 s	1711 s	C=O str.	1723	543	1730 vs	1744 s	C=O str.
1415	332	1461 m	1480 sh	HNC bend.	1435	351	1445 s	1470 s	HNC bend.
1397	13	1412 s	1443 s	CH_2 def.	1395	22	1402 m	1388 m	CH_2 def.
1241	22	1398 s	1382 s	N-C4 str. + skel. i.p.	1261	13	1321 mw	1312 m	HCS bend. + skel. i.p.
1192	105	1307 m	1305 m	skel. i.p.	1206	122	1213 m	1247 w	N-C4 str. + skel. i.p.
1147	4	1232 s	1234 s	N–C2 str.+ skel. i.p.	1146	0			HCS bend.+ HCSC tors.
1144	691	1163 s	1188 s	skel. o.p.	1120	649	1170 s	1177 vs	C=S str. + skel. i.p.
1045	120	1073 s	1084 s	C=S str. + skel. i.p.	1069	58	1153 s	1105 m	N-C2 str. + C=S str.
894	33	1032 m		skel. o.p.	871	17	895 vw		skel. o.p.
802	13	885 ms	887 s	skel. i.p.	807	10	864 vw		skel. i.p.
770	151	869 m	880 s	skel. o.p.	793	172		789 m	skel. o.p.
754	8	*	823 s	C5-S1 str.	722	34	*	752 m	C5-S1str.
646	14	798 s	786 s	C2-S1 str.	645	36	623 vw		C2-S1 str.
552	4	696 m	682 s	skel. o.p.	631	0			OCSC tors. + skel. i.p.
541	3	636 m		skel. o.p.	539	5	556 w	566 m	skel. i.p.
521	6	578 m	545 s	C2-N str. + skel. i.p.	486	10	498 w		skel. o.p.
468	41	492 m	514 s	skel. i.p.	431	32	446 w	456 s	skel. i.p.
396	7	485 m	425 s	skel. i.p.	397	3	415 vw	418 s	skel. i.p.
245	5		263 s	skel. i.p.	259	10		292 s	skel. i.p.
145	5		182 s	skel. o.p.	152	7		164 m	skel. o.p.
97	8		176 s	skel. o.p.	85	6			skel. o.p.

TABLE 4 (continued)

1	2	3	4	5	6	7	8	9	10
Thiazolidin-2,4-one **3**					Thiorhodanine **4**				
3492	116	3391m	3145 m, 3055 m	NH str.	3470	101	3365 mw	3086 m	NH str.
3009	1	*	2923 m	CH_2 as. str.	3013	3	*	2914 sh	CH_2 as. str.
2951	5	*	2831 w	CH_2 sym. str.	2954	7	*	2894 m	CH_2 sym. str.
1756	175	1755 m	1738 s	C4=O7 str.	1449	652	1437 vs	1496 s	HNC bend.
1711	738	1704 vs	1659 vs	C2=O6 str.	1395	20	1399 m	1386 s	CH_2 def.
1400	10	1406 w	1392 w	CH_2 def.	1277	49	1290 m	1282 s	HCS bend.
1360	22	1365 m	1343 s	HNC bend.	1178	275	1255 s	1189 vs	N–C5 str. + CNC bend.
1252	93	1326 s	1318 m	HCS bend. + N-C4 str.	1174	66	1212 m	1181 s	C2=S7 str. + skel. i.p. + C4=S7
1207	183	1130 m	1233 m	ring def.+ HCS bend.	1141	0			HCS bend.+ HCSC tors.
1150	3	*	~1100 sh	ring def.+ HCS bend.	1123	928	1120 vs		C2-N str. + ring def.
1108	169	*	1165 s	C2-N str. + ring def.	1008	305	1049 vs	1046 vs	C2=S7 str. + NCS bend. + C4=S7
899	40	894 w	893 m	skel. o.p.	865	15			skel. o.p.
818	3	*	~820 sh	skel. i.p.	808	122	873 vs	865 s	skel. o.p.
761	37	*	808 s	C5-S1 str. + ring def.	795	15			skel. i.p.
758	202	*	791 s	skel. o.p.	713	23	671 vs		C5-S1 str.
650	34	*	727 s	C2-S1 str. + ring def.	637	18	667 s		C2-S1 str.
629	5	612 w	619 m	skel. o.p.	548	7	612 m		skel. o.p.
583	0			skel. i.p.	479	1	545 w		skel. o.p.
546	3	544 w	576 vw	skel. o.p.	443	34	485 w		skel. i.p. + C2=S7
488	31	499 m	514 s	skel. i.p.	420	16	454 w		skel. i.p. + C4=S6
443	6	470 w	485 w	skel. i.p.	333	2			skel. i.p.
353	20	404 w	405 s	skel. i.p.	203	5			skel. i.p.
165	8		181 ms	skel. o.p.	132	2			skel. o.p.
91	7			skel. o.p.	89	7			skel. o.p.

* $CHCl_3$ absorption; i.p. – in plane; o.p. – out of plane.

An analysis of the theoretical spectra of rhodanine, isorhodanine, and thiorhodanine shows that the C=S stretching vibration is always coupled with the in-plane deformation vibrations of the five-membered ring. The bands for which this vibration contributes to the other normal modes are found to be in the region 1200-1000 cm^{-1} (Table 4). In contrast to them the C–S stretching vibrations in these compounds are characteristic. An exception is thiazolidine-2,4-dione where the C–S vibrations are coupled with the ring deformation coordinates (Table 4). In compounds **1**-**4** the bands due to the C–S stretching vibration were found to be located in the region 823-619 cm^{-1}.

Our study includes also thiorhodanine, whose IR spectra obviously indicate the presence of rhodanine, although its melting point coinsides well with that reported by Grishchuk [19]. This means that thiorhodanine decomposes during measurement of its IR spectrum because the rhodanine bands increase with the time. The strongly pronounced thiorhodanine instability has also been noticed by Grishchuk [19].

Lebedev and Yakimenko [20] have reported the presence of strong bands at 455, 417, 293, 165 and 163 cm^{-1} in the spectrum of isorhodanine. We observed such strong bands in the region 500-150 cm^{-1} in the IR spectra of rhodanine, isorhodanine, and thiazolidine-2,4-dione.

EXPERIMENTAL AND CALCULATIONS

Rhodanine (thiazolidin-4-one-2-thione) was synthesized according to Nencki [21] from monochloroacetic acid and ammonium thiocyanate. The product was recrystallized from water and dried in vacuum; mp 168-170°C. Thiazolidine-2,4-dione was synthesized according to Volhard [22] from monochloroacetic acid and thiourea. The product was recrystallized from water and dried in vacuum; mp 120-122°C. Isorhodanine (4-thioxothiazolidin-2-one) was synthesized according to Grishchuk et al. [23] from thiazolidine-2,4-dione and phosphorus pentasulfide in dioxane. The product was recrystallized from 1,2-dichloroethane and dried in vacuum; mp 158-162°C. Thiorhodanine (2,4-thiazolidinedithione) was synthesized according to Grishchuk [19] from rhodanine and phosphorus pentasulfide in dry dioxane. The product was recrystallized from methanol and dried in a desiccator in vacuum; mp 98-100°C.

The IR spectra of rhodanine, isorhodanine, thiazolidine-2,4-dione, and thiorhodanine were recorded with the Bruker IFS-113V FTIR spectrometer. Solid state spectra were taken in CsI pellet in the spectral region 4000-150 cm^{-1}. The spectra of saturated solutions in $CHCl_3$ were recorded in a 0.1 mm KBr cell in the spectral region 4000-400 cm^{-1}.

Ab initio calculations were performed by means of the GAMESS [24] program. The standard Dunning/Hay [25], 3-21G$^{(*)}$* [26, 27], 4-31G** [28-30] and 6-31G** [31, 32] basis sets were used at the Hartree-Fock level. The 3-21G$^{(*)}$* basis set places d-type Gaussian functions on the second-row sulfur atom only and on the hydrogen atoms. Additional single-point HF/6-31G**//HF/3-21G$^{(*)}$* calculations were then carried out. For tautomers **A** of compounds **1**-**4** geometry optimization was also carried out at the HF/6-31G** level. *Ab initio* geometry optimizations were done within C_1 symmetry and the gradient threshold was $1.0 \cdot 10^{-4}$ Hartree/Bohr. Subsequently, the effect of electron correlation was studied at the MP2/6-31G**//HF/3-21G$^{(*)}$* level. Single-point energies at the MP2 level [33] were calculated with frozen core MP2(fc).

Semiempirical MNDO [34, 35], AM1 [36, 37], MNDO-PM3 [38] methods were also used. The calculations were carried out with the MOPAC 6.0 program package [39]. The geometries of the investigated compounds were completely optimized using the EF [40] procedure. For all calculations the option PRECISE was used.

The IR frequencies and intensities for the most stable tautomers of compounds studied were computed at the HF/3-21G$^{(*)}$* level using the numerical derivative procedure incorporated in the GAMESS program. Calculated frequencies were scaled by a factor of 0.893 to correct for vibrational anharmonicity at the SCF level.

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