

Spectral properties and intramolecular hydrogen bonds of 2,4- and 2,5-disubstituted 3-oxo-2*H*-pyridazine-5- and -4-thiols

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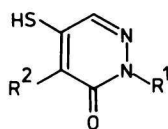
*Dedicated to Associate Professor Ing. F. Hanic, DrSc.,
in honour of his 60th birthday*

Infrared, ultraviolet spectral data and pK_a values of sixteen 2,4-disubstituted 3-oxo-2*H*-pyridazine-5-thiols and 2,5-disubstituted 3-oxo-2*H*-pyridazine-4-thiols are reported. Intramolecular hydrogen bonds of these compounds are discussed; relatively strong intramolecular S—H...O and S—H...S hydrogen bonds were found which are due to the ring size and the presence of the C=O group of the pyridazine ring.

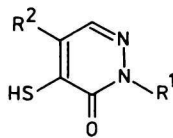
Приводятся результаты ИК-, УФ-спектроскопического исследования и величины pK_a шестнадцати 2,4-дизамещенных 3-оксо-2*H*-пиридазин-5-тиолов и 2,5-дизамещенных 3-оксо-2*H*-пиридазин-4-тиолов. Обсуждаются внутримолекулярные водородные связи в данных соединениях; были обнаружены относительно прочные внутримолекулярные S—H...O и S—H...S водородные связи, связанные с размером цикла и присутствием C=O группы в пиридазиновом цикле.

It is known that the protondonating property of the S—H group by the S—H...B intermolecular hydrogen bond formation is due to its acidic properties. With increasing acidity of the —S—H group the strength of the S—H...B hydrogen bond is similarly increased as it is with the O—H...B hydrogen bonds. The S—H...B hydrogen bonds are significantly weaker than the O—H...B hydrogen bonds [1—6]. The intensity of the ν (S—H) bands, measured in solvents with which thiols cannot form hydrogen bonds, is very low [7, 8], therefore, it has been presumed for a long time that thiols do not form hydrogen bonds. The intensity of the ν (S—H) bands is significantly increased if the measurements are carried out in protonaccepting solvents [9—11].

Pyridazinone thiols investigated were used as starting compounds in the synthesis of organophosphoric acids used as pesticides [12]. In the infrared spectra of compounds investigated of the formula

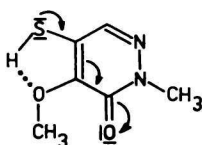


I—XIII
A

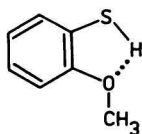


XIV—XVI
B

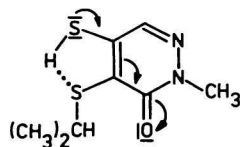
one or two medium intense $\nu(\text{S—H})$ bands are observed in the region of $\tilde{\nu} = 2492\text{—}2585\text{ cm}^{-1}$ (Table 1) pointing to the presence of intramolecular $\text{S—H}\cdots\text{O}$ and $\text{S—H}\cdots\text{S}$ hydrogen bonds. In comparison with 2-substituted thiophenols containing the RO— , RS— , OH— , and SH— groups the wavenumbers of the $\nu(\text{S—H})$ bands of all compounds investigated are lower, which could be explained by conjugation effects increasing the acidity of the S—H group



$\tilde{\nu}(\nu(\text{S—H}))$: 2585 cm^{-1}
 $\sigma(\text{S—H})$: 3.95 ppm



2593 cm^{-1}
3.66 ppm



2492 cm^{-1}
4.23 ppm

The $\nu(\text{S—H})$ bands of compounds *X* and *XI* containing the CH_3S and $(\text{CH}_3)_2\text{CHS}$ groups are observed at lower wavenumbers than those of compounds *I—IX*, which is evidently connected with a formation of a stronger hydrogen bond. This fact is also in agreement with higher chemical shifts of the S—H protons. Approximately equal wavenumbers of the $\nu(\text{S—H})$ bands of compounds *IX*, *X*, and *XVI* point to the approximately equal strength of the $\text{S—H}\cdots\text{S}$ and $\text{S—H}\cdots\text{O}=\text{C} <$ intramolecular hydrogen bonds. The intensities of the $\nu(\text{S—H})$ bands of compounds studied are higher when compared with those of thiophenols, which could be explained by the presence of the carbonyl group (Table 3).

Significantly lower wavenumbers of the $\nu(\text{C}=\text{O})$ bands in the spectra of compounds *XII—XVI* as compared with those of compounds *I—XI* are connec-

Table 1

IR and ¹H NMR spectral data of 2,4-disubstituted 3-oxo-2*H*-pyridazine-5-thiols (*A*) and 2,5-disubstituted 3-oxo-2*H*-pyridazine-4-thiols (*B*) in CCl₄

Compound	R ¹	R ²	$\tilde{\nu}/\text{cm}^{-1}$				$\delta(\text{S—H})/\text{ppm}$
			CCl ₄		CHCl ₃		
			$\nu(\text{C=O})$	$\nu(\text{S—H})$	$\nu(\text{S—H})$	$\log(\epsilon/(\text{m}^2 \text{mol}^{-1}))$	
<i>I</i>	CH ₃	CH ₃ O	1650	2585	2586	3.56	3.95
<i>II</i>	C ₆ H ₁₃ (cyclo)	CH ₃ O	1647	2584	2585	3.21	3.91
<i>III^F</i>	C ₆ H ₅	CH ₃ O	1663.5	2585	2585	3.23	3.86
<i>IV</i>	3-CH ₃ C ₆ H ₄	CH ₃ O	1663	2585	2586	—	—
<i>V^a</i>	3-ClC ₆ H ₄	CH ₃ O	1665	2583	2584	—	—
<i>VI</i>	3-CF ₃ -4-ClC ₆ H ₃	CH ₃ O	1665	2582	2584	—	—
<i>VII</i>	C ₆ H ₅	C ₂ H ₅ O	1663	2585	2586	3.21	—
<i>VIII</i>	CH ₃	C ₃ H ₇ O	1651	2587	2585	3.18	3.96
<i>IX</i>	C ₆ H ₅	<i>i</i> -C ₃ H ₇ O	1662	2585	2585	3.14	4.03
<i>X</i>	C ₆ H ₅	C ₂ H ₅ S	1665	2492	2492	3.36	4.16
<i>XI</i>	CH ₃	<i>i</i> -C ₃ H ₇ S	1652	2493	2492	3.85	4.23
<i>XII</i>	CH ₃	SH	1636	2492	2493	4.05	4.21
<i>XIII^F</i>	C ₆ H ₅	SH	1647	2500	2490	3.89	4.19
				2480			
<i>XIV</i>	CH ₃	CH ₃ O	1635	2520	2492	3.29	4.16
				2492			
<i>XV</i>	C ₆ H ₅	CH ₃ O	1647	2518	2490	3.11	—
				2483			
<i>XVI</i>	CH ₃	C ₂ H ₅ S	1647	2493	2496	3.23	4.17

a) Measured in CHCl₃.

Table 2
 Ultraviolet spectral data and pK values of substituted 3-oxo-2H-pyridazine thiols

Compound	λ_{\max}/nm $\log(\epsilon/(\text{m}^2 \text{mol}^{-1}))$											pK _a λ_{\max}/nm
	Methanol			Water				Dioxan				
<i>I</i>	230.5	255	285		224	252	290 sh	325	236	280	302	3.01
	3.12	2.79	2.72		3.05	3.15	(2.73)	2.87	3.14	2.72	2.72	284.5
<i>II</i>	231.5	248	287	326 sh	225	250	295 sh	320	235	280	303	3.31
	3.11	3.02	2.78	(2.76)	3.01	3.55	(2.75)	2.81	3.23	2.78	2.69	322
<i>III</i>	230	263	290	344 sh	214	257	300 sh	333	233.5	—	300	3.27
	3.20	3.02	2.91	(2.76)	3.06	3.08	(2.75)	2.85	3.21	—	2.96	325
<i>IV^a</i>	233	265	292	342 sh	226	255	297 sh	333	237	—	297	—
	3.18	3.24	2.94	(3.00)	3.12	3.26	(2.86)	3.02	3.27	—	2.96	—
<i>VI</i>	240	268	296	351 sh	219	258	296 sh	338	240	—	302	—
	3.22	3.19	3.05	(2.99)	3.22	3.23	2.90	3.02	3.15	—	3.05	—
<i>VII</i>	235	263	294		227	256	298 sh	330	235	—	294	—
	3.24	3.09	2.98		3.06	3.13	(2.86)	2.94	3.26	—	2.99	—
<i>VIII</i>	234	262	293	342 sh	220	256	300 sh	333	236	290	320 sh	2.95
	3.18	3.19	2.96	(2.79)	2.96	3.13	(2.72)	2.86	3.18	2.87	2.62	333

Table 2 (Continued)

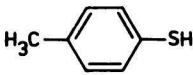
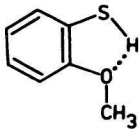
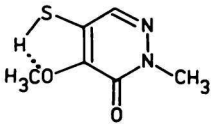
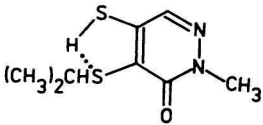
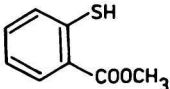
Compound	λ_{\max}/nm $\log \{\epsilon/(\text{m}^2 \text{mol}^{-1})\}$											pK_a λ_{\max}/nm
	Methanol				Water				Dioxan			
<i>IX</i>	234	262	293	342	—	256	297 sh	333	241	—	305	3.20
	3.18	3.19	2.96	2.79		3.24	2.87	2.99	3.26		3.00	3.37
<i>X</i>	224	253	272	317	229	263	317	351	238	—	325	3.49
	3.90	3.03	2.99	2.90	2.97	3.18	2.87	2.89	3.11		2.97	3.51
<i>XI</i>	245	263	300	325 ^b	220	260	294 sh	357	243	302	315 ^c	3.35
	3.18	3.15	2.82	2.93	2.95	3.17	2.38	2.95	3.05	2.82	2.85	3.57
<i>XII</i>	218.5	262	306	350 sh	257	—	302	347	225	362	380 sh	2.78
	3.11	3.26	2.75	(2.79)	3.07		2.73	2.85	3.00	2.90	(2.00)	3.50
<i>XIV</i>	225	—	314	357	224	313	325	348	227	310	320 ^d	4.46
	3.10		2.78	2.56	3.12	2.76	2.72	2.62	3.06	2.83	2.85	3.47
<i>XV</i>	220	258	—	364	207	220	257 sh	359	230	287 sh	325	4.56
	3.31	2.82		2.94	3.36	3.28	(2.82)	2.85	3.19	2.71	2.86	3.57
<i>XVI</i>	208	257	302	349	215	248	298	353	243	297	340 ^e	3.02
	3.02	3.11	2.70	2.81	3.05	2.93	2.69	2.80	3.02	2.80	2.71	3.48

a) In methanol and dioxan.

Additional bands: b) at $\lambda_{\max} = 338 \text{ nm}$ ($\log \{\epsilon\} = 2.92$); c) at $\lambda_{\max} = 325 \text{ nm}$ ($\log \{\epsilon\} = 2.86$); d) at $\lambda_{\max} = 335 \text{ nm}$ ($\log \{\epsilon\} = 2.58$); e) at $\lambda_{\max} = 355 \text{ nm}$ (sh) ($\log \{\epsilon\} = 2.61$). Values in brackets are approximate.

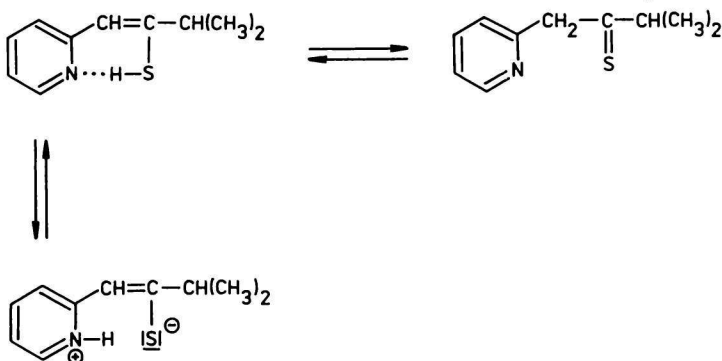
Table 3

Comparison of the $\nu(\text{S—H})$ band intensities of the alkanethiols and thiophenols and compounds studied

Thiol	$\log(\epsilon/(\text{m}^2 \text{mol}^{-1}))$		Ref.
	CCl_4	CHCl_3	
$\text{CH}_3\text{CH}_2\text{—SH}$	0.08	—	[10]
	0.32	0.69	[11]
	3.45	2.94	[11]
	3.69	3.56	This paper
	4.12	3.85	This paper
	3.33	1.59	[11]

ted with a formation of the $\text{S—H}\cdots\text{O}=\text{C}<$ intramolecular hydrogen bond (Table 1). Also, from ultraviolet spectral data (Table 2) it appears that compounds *XII—XVI* absorb at longer wavelengths than compounds *I—XI*, which is in agreement with infrared spectral data of compounds investigated (Table 3). In the ^1H NMR spectra of compounds studied (Table 1) signals of the S—H protons are observed in the region of $\delta = 3.86\text{—}4.23$ ppm (*I—XI*) and $\delta = 4.16\text{—}4.21$ ppm (*XII—XVI*). Higher δ values of compounds studied in comparison with those of 2-substituted thiophenols can be explained by conjugation effects increasing the acidity of the SH group.

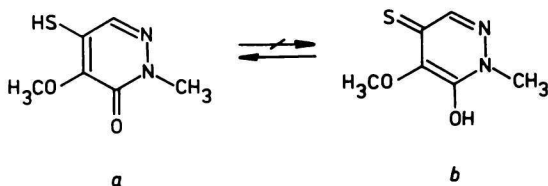
It is known that thiolic forms of some sulfur compounds form very strong intramolecular hydrogen bonds due to a proton transfer [13] (Scheme 1).



Scheme 1

Chemical shifts of the S—H protons of these types of compounds are observed at extremely high δ values ($\delta \approx 18$ ppm). High differences in pK_a values of compounds *I—XI* ($pK_a = 2.95—3.49$) and compounds *XIV—XVI* ($pK_a = 4.46—4.56$) (Table 2) can be explained by conjugation effects which play more significant role with compounds *I—XIII*.

In consequence of conjugation effects a formation of tautomeric enol form *b* can be considered with compounds *I—XIII*



The presence of the $\nu(\text{C}=\text{O})$ band and the absence of the $\nu(\text{O}—\text{H})$ band in the infrared spectra of compounds studied eliminates the tautomeric form *b*. This fact can be explained as follows:

1. The formation of the thione form *b* would cause the loss of the planarity of the ring resulting in the decrease of conjugation energy.
2. The thiol form *a* is stabilized by the intramolecular S—H \cdots O or S—H \cdots S hydrogen bond.

Evidently, the tautomeric form *b* is also stabilized by the intramolecular O—H \cdots O or O—H \cdots S hydrogen bonds which are stronger than the intramolecular S—H \cdots O or S—H \cdots S hydrogen bonds [14]



From the above mentioned it appears that the formation of the planar system is a decisive factor for higher stability of the tautomer *a*.

Experimental

Infrared spectra of compounds studied were recorded with a Unicam SP 100 instrument. The wavenumber calibration was checked against the spectrum of polystyrene. The spectra were recorded in tetrachloromethane and trichloromethane ($c \approx 0.04 \text{ mol dm}^{-3}$, cell thickness 2.6 mm). Ultraviolet spectra were recorded with a UV VIS (Zeiss, Jena) instrument, in methanol, water, and dioxan ($c = 1 \times 10^{-5} - 5 \times 10^{-5} \text{ mol dm}^{-3}$, cell thickness 1 cm). pK_a Values were determined by UV spectroscopy in a Britton—Robinson buffer solution at 25°C. $^1\text{H NMR}$ spectra were recorded with a Jeol FX-60 instrument in trichloromethane using tetramethylsilane as an internal standard. Synthesis of compounds investigated was described in [15].

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