SPECTRAL PROPERTIES AND INTRAMOLECULAR HYDROGEN BONDING IN 1-METHYL(PHENYL)-4(5)-SUBSTITUTED 6-OXO-1*H*-PYRIDAZIN-4(5)-OLS

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Infrared, ultraviolet and ^{1}H-NMR spectral data of 53 1-methyl(phenyl)-4(5)-substituted 6-oxo-1*H*-pyridazin-4(5)-ols are listed. Intramolecular hydrogen bondings are discussed; relatively strong hydrogen bondings OH···S were found, which are comparable in terms of strength with those of OH···O=C. Wavenumbers of ν(C=O) and ν(O—H) bands linearly correlated with substituent constants σ^*, σ_R and σ^F.

Pyridazinones under study were the starting material for the synthesis of esters of organophosphorus acids used as pesticides[1-4]. A linear correlation of ν(C=O) and ν(C=C) bands was already observed with pyridazin-4-yl esters of thiophosphoric acid[5].

The title pyridazinones revealed linear wavenumber correlations of ν(C=O) and ν(OH) bands with substituent constants with the exception of pyridazinones containing an SR group; the latter showed very strong intramolecular hydrogen bondings OH···SR.

Excepting sulfur containing compounds *IX–XII*, *XVIII* and *XIX* (Table I), pyridazinones *A* displayed absorption bands at about 3500 cm^{-1}, indicating the formation of intramolecular hydrogen bonding OH···OR, or OH···Hal. As known, the strength of an intramolecular hydrogen bonding first of all depends on the electronegativity of the electron-accepting group, charge of the donating or accepting groups, steric effects and on the resonance stabilization of the ring formed by the hydrogen bonding[6-8]. On the basis of wavenumbers of OH bond following order of the hydrogen-bonding strength was observed:

$$\mathrm{OH}\cdots\mathrm{S} > \mathrm{OH}\cdots\mathrm{O{=}C} > \mathrm{OH}\cdots\mathrm{O}\text{—} > \mathrm{OH}\cdots\mathrm{Hal}$$

Although oxygen atom is a more convenient proton acceptor than sulfur, still the ν(O—H) bands were observed at lower wavenumbers; this phenomenon can be rationalized by a stronger interaction of free electron pairs of the bulkier sulfur atom

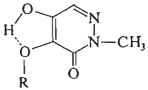
TABLE I

Wavenumbers of Bands in the IR Spectra (cm^{-1}) of Pyridazinones of General Formula *B* (in $CHCl_3$)

Compound	R^1	R^2	ν(C=N)	ν(C=O)	ν(O—H)
I[a]	H	CH_3	1 605	1 638	3 590
II[a]	Br	CH_3	1 622	1 633	3 510
III[a]	Cl	CH_3	1 615	1 631	3 510
IV[a]	HO	CH_3	1 622	1 660	3 382
V	CH_3O	CH_3	1 630	1 646	3 508
VI	C_2H_5O	CH_3	1 629	1 645	3 508
VII	$n\text{-}C_3H_7O$	CH_3	1 627	1 644	3 509
VIII	$i\text{-}C_3H_7O$	CH_3	1 626	1 644	3 505
IX	CH_3S	CH_3	1 635	1 660	3 375
X	C_2H_5S	CH_3	1 634	1 659	3 370
XI	$n\text{-}C_3H_7S$	CH_3	1 635	1 660	3 370
XII[a]	$i\text{-}C_3H_7S$	CH_3	1 623	1 656	3 365
XIII	Cl	C_6H_5	1 615	1 652	3 510
XIV	CH_3O	C_6H_5	1 637	1 660	3 508
XV	C_2H_5O	C_6H_5	1 635	1 658	3 517
XVI	C_6H_5O	C_6H_5	1 635	1 667	3 519
XVII	$C_6H_5OCH_2CH_2O$	C_6H_5	1 642	1 655	3 490
XVIII	CH_3S	C_6H_5	1 647	1 658	3 370
XIX	C_2H_5S	C_6H_5	1 647	1 660	2 368
XX[b]	$(CH_3)_2C=NO$	C_6H_5	1 622	1 633	3 400
XXI	CH_3O	C_2H_5	1 629	1 645	3 508
XXII	CH_3O	$n\text{-}C_3H_7$	1 627	1 646	3 509
XXIII	CH_3O	$i\text{-}C_3H_7$	1 629	1 644	3 508
XXIV	CH_3O	$n\text{-}C_4H_9$	1 629	1 645	3 508
XXV	CH_3O	$n\text{-}C_5H_{11}$	1 627	1 645	3 506
XXVI	CH_3O	$n\text{-}C_6H_{13}$	1 628	1 647	3 508
XXVII	CH_3O	C_6H_{11}-cyclo	1 626	1 644	3 506
XXVIII	CH_3O	$C_6H_5CH_2$	1 629	1 651	3 518
XXIX	CH_3O	$CH_2=CHCH_2$	1 630	1 645	3 505
XXX[b]	Cl	C_2H_5	1 608	1 640	—
XXXI	Cl	$n\text{-}C_3H_7$	1 620	1 654	3 500
XXXII[b]	Cl	$i\text{-}C_3H_7$	1 618	1 644	3 500
XXXIII	Cl	$n\text{-}C_4H_9$	1 621	1 653	3 501
XXXIV	Cl	$n\text{-}C_5H_{11}$	1 615	1 646	3 505
XXXV	Cl	$n\text{-}C_6H_{13}$	1 617	1 647	3 503
XXXVI[b]	Cl	$CH_2=CHCH_2$	1 619	1 655	3 500
XXXVII[b]	Cl	$C_6H_5CH_2$	1 633	1 655	—
XXXVIII[b]	Cl	$C_2H_5SCH_2$	1 621	1 643	—
XXXIX[b]	Cl	C_6H_{11}-cyclo	1 615	1 645	—
XL[b]	Cl	$C_2H_5OCH_2$	1 609	1 648	—

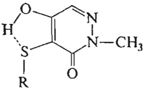
[a] Saturated solution; [b] measured in KBr.

with the hydrogen atom of the OH group, when compared with oxygen, *e.g.* compounds *I*, *VI* and *X*.



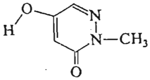
ν(OH) 3508 cm⁻¹

VI



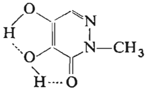
3370 cm⁻¹

X



3590 cm⁻¹

I



ν(OH) 3382 cm⁻¹

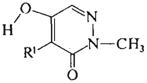
IV

The IR spectrum of *I* contained the ν(O—H) band at 3590 cm^{-1}, backing thus the assignment of these bands to other compounds under investigation. This also might be in relation with intramolecular hydrogen bondings of *o*-halogen-substituted phenols. No intramolecular hydrogen bonding was observed with *o*-fluorophenol due to a too long distance of OH···F. The same holds for compounds *I*–*VIII*, where the distance OH···O is also relatively great as to a strong intramolecular hydrogen bonding could be formed; consequently, the wavenumber of ν(OH) bands appeared at ~3500 cm^{-1} with exception of compound *IV*. Here is a possibility two types of intramolecular bondings to be formed, where the OH···O=C bond is stronger than that of OH···OR.

The spectrum of *IV* displayed only one broad band, although two bands could be expected (at ~3500 and 3300 cm^{-1}); this was caused by overlapping. The length of the carbon chain of RO—, or RS groups affected relatively little the wavenumber of ν(OH···O) and ν(OH···S) bands. The value ε of ν(O—H) was found virtually not to alter with compounds *V* and *IX* in the concentration range $2 . 10^{-2}$ to $2 . 10^{-3}$M in chloroform (*V*, $\varepsilon = 142 \rightarrow 145$ l mol^{-1} cm^{-1}; *IX*, $\varepsilon = 71 \rightarrow 72$ l mol^{-1} cm^{-1}) this being an evidence that an intramolecular hydrogen bonding was involved.

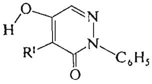
The wavenumber of ν(C=O) bands of compounds, excepting sulfur containing ones, lowers by 15 cm^{-1} when tetrachloromethane was replaced by chloroform. The wavenumber of ν(C=O) bands of sulfur containing compounds *IX*–*XII* and *XVIII*–*XXX* is less affected than that of other compounds of *A* type (~6 cm^{-1} lower wavenumber in $CHCl_3$ than in CCl_4); this finding can be explained by a steric interaction of the SR group adjacent to carbonyl group.

Compounds of general formula *B* (Table II) had, due to intramolecular hydrogen bonding, the wavenumber of ν(C=O) bands less affected as anticipated by the kind of solvent by ~5 cm^{-1}; wavenumbers of ν(C=O) bands were shifted towards lower values when changing CCl_4 to $CHCl_3$. Higher wavenumbers of ν(C=O) bands were observed with compounds *XIII*–*XX*, when compared with those of *I*–*XII* with the same substituents R^1, what can be rationalized by a lowered conjugation of the carbonyl group resulting from the withdrawal of π-electrons of the benzene ring and the lone electron pair of oxygen of the carbonyl group. This accorded with ultraviolet spectra of these compounds. Wavenumbers of ν(C=O) bands of *V*–*VIII* were lower (~1 645 cm^{-1}) than those of *XLI*–*XLIII* (~1 660 cm^{-1}) having an intramolecular hydrogen bonding HO···O=C. This indicated that the +M effect of hydroxyl group was decisive for the wavenumber of ν(C=O) bands. Sulfur containing compounds *IX*–*XII* and *XLIV* to *XLVI* behaved inversely. The strongest electron-donating effect showed the RS



λ_{max} 286–287 nm

IV–*VIII*



λ_{max} 272–283 nm

XIV–*XVII*

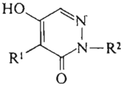
TABLE II

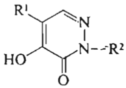
Wavenumbers of Bands in the IR Spectra (cm^{-1}) of Pyridazinones of General Formula *B* (in $CHCl_3$)

Compound	R^1	R^2	ν(C=N)	ν(C=O)	ν(O—H)
XLI	CH_3O	CH_3	1 609	1 662	3 375
XLII	C_2H_5O	CH_3	1 619	1 660	3 386
XLIII	n-C_3H_7O	CH_3	1 618	1 660	3 385
XLIV	CH_3S	CH_3	1 619[a]	1 635	3 375
XLV	C_2H_5S	CH_3	1 620	1 632	3 370
XLVI	n-C_3H_7S	CH_3	1 620[a]	1 635	3 372
XLVII	Cl	CH_3	1 620[a]	1 630	3 380
XLVIIII	Br	CH_3	1 610[a]	1 630	3 380
IL	CH_3O	C_6H_5	1 625	1 665	3 375
L	C_2H_5O	C_6H_5	1 625	1 665	3 375
LI	CH_3S	C_6H_5	1 612	1 635	3 375
LII	C_2H_5S	C_6H_5	1 615	1 635	3 370
LIII	Cl	C_6H_5	1 600	1 645	3 370

[a] Values are approximate.

group bound at position 4. The wavenumbers of ν(O—H) bands conjugated through an intramolecular hydrogen bonding with sulfur of the RS group and oxygen of the carbonyl group are very close ($\sim 3370\,\text{cm}^{-1}$), what indicated an approximately equally strong hydrogen bonding; this finding is, with respect to the ability of sulfur to form hydrogen bondings, quite surprising.





The wavenumbers of ν(C=N), ν(C=O) and ν(O—H) bands were correlated with σ^*, σ^F, σ_I and σ_R constants of substituents[9]. Substances *I*–*IX* showed a linear correlation between the wavenumber of ν(O—H) bands and substituent R¹ constants with σ^F constants; correlation coefficients were lower with σ_R and σ_I:

$$\nu(\text{O—H}) - \sigma^F: \varrho = 3{\cdot}43,\ r = 0{\cdot}86$$

$$\nu(\text{O—H}) - \sigma_R: \varrho = -3{\cdot}06,\ r = 0{\cdot}72$$

$$\nu(\text{O—H}) - \sigma^*: \varrho = 2{\cdot}56,\ r = 0{\cdot}66$$

$$\nu(\text{O—H}) - \sigma_I: \varrho = 1{\cdot}28,\ r = 0{\cdot}66$$

Sulfur containing compounds *IX*–*XII* could not be included into the correlation, since the wavenumbers of ν(O—H) bands were observed, due to a strong intramole-

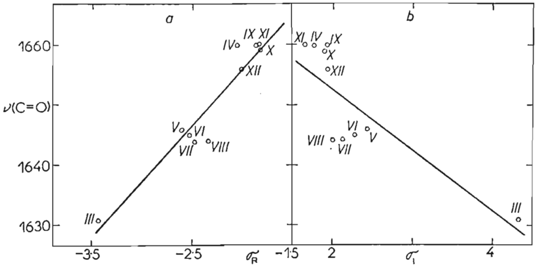


FIG. 1

Dependence of ν(C=O) Both on σ_I (*b*) and σ_R (*a*) in 5-Substituted 1-Methyl-6-oxo-1*H*-pyridazines cular hydrogen bonding, at about 3370 cm^{-1}. A like linear correlation was learned from the relation of wavenumbers of $\nu(C{=}O)$ bands with σ_I and σ_R constants (Fig. 1):

$$\nu(C{=}O) - \sigma_I: \varrho = -10{\cdot}53, r = 0{\cdot}83$$

$$\nu(C{=}O) - \sigma_R: \varrho = 18{\cdot}80, r = 0{\cdot}96$$

The correlation coefficients were found to be lower, when correlating the wavenumbers of $\nu(C{=}N)$ bands with σ_I and σ_R constants:

$$\nu(C{=}N) - \sigma_I: \varrho = 5{\cdot}28, r = 0{\cdot}64$$

$$\nu(C{=}N) - \sigma_R: \varrho = 9{\cdot}03, r = 0{\cdot}71 .$$

Compounds *XIII*–*LIII* did not display linear dependence of $\nu(C{=}O)$ and $\nu(C{=}N)$ bands on substituent constants when correlating the wavenumbers of $\nu(C{=}O)$, $\nu(C{=}N)$ and $\nu(O{-}H)$ bands with substituent constants.

Ultraviolet spectra of these compounds (Table III) were characteristic of two bands; the band at a shorter wavelength had a shoulder. The position of bands at shorter wavelengths (210–222 nm) is relatively little affected by the nature of R^1 and R^2 substituents with the exception of *I* and *LIII*–*LV* in the spectra of which bands at 252 and 247 and 257 nm, respectively were seen. Bands at longer wavelengths were not significantly affected by the nature of substituents R^1 and R^2. Compounds containing sulfur and *XX*, *LIII* constituted an exception; here the bands at 300–318 nm were observed, this being obviously associated with a stronger intramolecular hydrogen bonding OH···SR, or with the nature of substituents $(CH_3)_2C{=}NO$ and Cl. Bands at lower wavelengths belonged to $\pi^* \leftarrow \pi$ transitions, whereas those at the longest wavelengths to $\pi^* \leftarrow n$ transitions.

Signals of =CH protons of the pyridazinone ring were seen in the ^{1}H-NMR spectra at δ 7·55–8·01 ppm. The nature of the substituent little affected the chemical shifts of these protons. Chemical shifts of =CH protons of the pyridazinone ring of *XIII*–*XX* and *IL*–*LIII* had higher δ values than the other compounds, what indicated that the lone electron pair of the nitrogen atom of the pyridazinone ring is in interaction with π-electrons of benzene ring; as a consequence, a shielding of =CH protons took place.

EXPERIMENTAL

The infrared spectra were measured with a UR-20 (Zeiss, Jena) spectrometer in $CHCl_3$ at 0·02 to 0·06M concentrations and 0·0089 cm-cell width. Spectra of little soluble compounds were measured either as saturated solutions in $CHCl_3$, or in KBr disc. Reading accuracy ±1 cm^{-1}.

TABLE III

Ultraviolet (λ in nm, ε in l mol cm^{-1}) and ^{1}H-NMR (δ, ppm) Spectral Data of Pyridazinones

Compound	λ max (log ε)	λ max (log ε)	λ max^a	CH$_3$N^b	=CH—^{b}	
I	252 (4·02)	282 (3·93)	—	3·55 s	7·60 d	6·01 d
II	214 (4·38)	291 (3·68)	—	3·62 s	7·61 s	
III	214 (4·18)	287 (3·61)	—	3·60 s	7·67 s	
IV	215 (4·31)	286 (3·71)	—	3·67 s	7·85 s	7·55 s
V	214 (4·50)	285 (3·75)	224	3·52 s	7.60 s	
				3·74 s^c	7·67 s^c	
VI	214 (4·42)	286 (3·72)	—	3·63 s	7·60 s	
VII	215 (4·49)	287 (3·71)	—	3·65 s	7·58 s	
VIII	214 (4·37)	287 (3·71)	225	3·64	7.66 s	
IX	215 (4·23)	318 (3·72)	228	3·70 s	7·58 s	
X	214 (4·24)	317 (3·70)	225	3·72 s	7·57 s	
				3·80 s^c	7·80 s^c	
XI	213 (4·21)	318 (3·74)	228	3·55 s	7·56 s	
XII	214 (4·21)	317 (3·70)	227	3·59 s	7·57 s	
XIII	211 (4·22)	285 (4·01)	236	—	7·96 s	
XIV	210 (4·41)	283 (3·91)	223	—	7·76 s	
XV	211 (4·40)	281 (3·82)	227	—	7·77 s	
XVI	211 (4·48)	284 (3·87)	226	—	7·77 s	
XVII	210 (4·38)	272 (8·82)	220	—	7·76 s	
XVIII	212 (4·23)	310 (3·73)	232	—	7·78 s	
XIX	210 (4·31)	313 (3·79)	244	—	7·78 s	
XX	212 (4·25)	302 (4·06)	233	—	7·76 s	
XXI	220 (4·42)	285 (3·63)	—	3·81 s^d	7·65 s	
XXII	215 (4·31)	290 (3·63)	—	3·82 s^d	7·66 s	
XXIII	220 (4·40)	285 (3·63)	—	3·80 s^d	7·70 s	
XXIV	215 (4·26)	284 (3·63)	—	3·81 s^d	7·63 s	
XXV	215 (4·39)	282 (3·58)	—	3·82 s^d	7·65 s	
XXVI	221 (4·31)	285 (3·73)	—	3·57 s^d	7·16 s	
XXVII	215 (4·45)	286 (3·66)	—	3·80 s^d	7·63 s	
XXVIII	214 (4·49)	286 (3·76)	228	3·85 s^d	7·70 s	
XXIX	218 (4·31)	289 (3·88)	—	3·85 s^d	7·75 s	
XXX	216 (4·45)	286 (3·76)	227	—	7·77 s	
XXXI	215 (4·46)	286 (3·76)	227	—	7·72 s	
XXXII	215 (4·50)	286 (3·75)	226	—	7·70 s	
XXXIII	216 (4·42)	287 (3·73)	227	—	7·71 s	
XXXIV	216 (4·51)	287 (3·73)	227	—	7·72 s	
XXXV	216 (4·47)	286 (3·71)	227	—	7·75 s	
XXXVI	215 (4·45)	286 (3·77)	227	—	7·75 s	
XXXVII	216 (sh)	280 (4·05)	227	—	7·76 s	
XXXVIII	222 (sh)	287 (4·31)	298^e	—	7·88 s	
XXXIX	217 (4·53)	280 (3·92)	227	—	7·72 s	

TABLE III
(*Continued*)

Compound	λ max (log ε)	λ max (log ε)	λ max[a]	CH$_3$N[b]	=CH—[b]
XL	215 (4·49)	287 (3·82)	226	—	7·75 s
XLI	218 (4·35)	288 (3·94)	205	3·60 s	7·81 s
XLII	218 (4·32)	287 (3·91)	—	3·61 s	7·76 s
XLIII	218 (4·32)	288 (3·91)	205	3·60 s	7·78 s
XLIV	215 (4·17)	306 (3·75)	208	—	—
XLV	215 (4·11)	303 (3·82)	—	3·83 s	7·60 s
XLVI	215 (4·19)	308 (3·75)	202	—	—
XLVII	217 (4·35)	288 (3·95)	205	3·61 s	7·80 s
XLVIII	218 (4·22)	284 (3·71)	—	3·61 s	7·83 s
IL	222 (4·35)	285 (3·79)	—	—	8·01 s
L	222 (4·35)	285 (3·69)	—	—	8·00 s
LI	214 (4·28)	291 (3·81)	232[f]	—	7·92 s
LII	215 (4·32)	295 (3·71)	232[g]	—	8·04 s
LIII	247 (4·27)	300 (4·00)	—	—	7·96 s

[a] shoulder; [b] s singlet, d doublet; [c] measured in CDCl$_3$; [d] signals of CH$_3$O protons; [c] log ε 4·04; [f] log ε 4·28; [g] log ε 4·36.

Correlation of wavenumbers of ν(C=O), ν(C=N) and ν(O=H) bands with substituent constants was calculated with a Hewlett–Packard calculator. Ultraviolet spectra were recorded with a Specord UV VIS (Zeiss, Jena) apparatus in methanol at 3 . 10^{-5} and 7 . 10^{-5}M concentrations in a 1 cm-cell. The ^{1}H-NMR spectra were taken in deuteriated dimethyl sulfoxide and chloroform with a Tesla BS 487 C instrument operating at 80 MHz, hexamethyldisiloxane being the internal reference substance. Measured were chromatographically pure substances, the preparation of which was already published[10].

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