Tautomerism of Substituted 2*H*-1,2,6-Thiadiazin-3-one 1,1-Dioxides: ^{1}H, ^{13}C, and ^{15}N Nuclear Magnetic Resonance Studies

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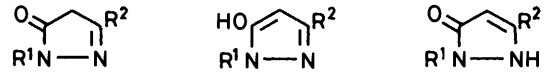
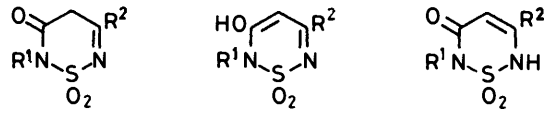
Tautomerism of 2,5-disubstituted (**4**), 4,5,6-substituted (**5**), and 5-substituted 2*H*-1,2,6-thiadiazin-3-one 1,1-dioxides (**6**) has been studied by u.v., ^{1}H, ^{13}C and natural-abundance ^{15}N n.m.r. spectroscopies. The effect of solvent concentration, temperature, and the nature of the substituents on the K_T variation has been investigated. Comparison between the tautomeric behaviour of 2*H*-1,2,6-thiadiazin-3-one derivatives and the related pyrazol-5-ones provides some conclusions about the role of aromaticity on the stability of the different tautomers.

The tautomerism of heterocyclic amides (lactams) is the result of two opposing effects (i) the tendency of the amide function to exist as such (and not in the imidate lactim form) and (ii) the aromaticity of the hydroxy tautomer.[1] This is exemplified in the pyridone tautomerism and it has been used to study the aromaticity of pyridines.[2] The commonest method to separate both effects is to use non-aromatic analogues as models, *e.g.* tetrahydropyridones.[2]



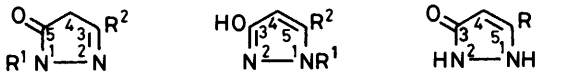
A B C

In the case of five-membered heterocycles, the problem is complex *e.g.* the pyrazol-5(4*H*)-ones[1] can exist in three tautomeric forms, A, B and C, that are commonly called CH, OH, and NH, respectively. Although there is a model for the A form [the corresponding pyrazolidin-5(4*H*)-ones], there is no obvious choice for the C form. We wish to report in this work a different approach; to interrupt the conjugation of the B form by intercalation of an SO_2 group between the two nitrogen atoms.



A B C

By comparing the tautomeric behaviour of 1,2,6-thiadiazin-one 1,1-dioxides to that of the pyrazolones it is possible to determine the role of the aromaticity on the stability of the NH-tautomer C.

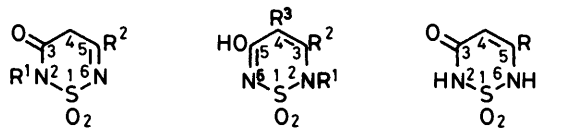


(**1**) (**2**) (**3**)

a; R^1 = Ph, R^2 = Me
b; R^1 = R^2 = Me
c; R^1 = *n*-Bu, R^2 = Me
d; R^1 = *n*-Bu, R^2 = NH_2

a; R^1 = C_6H_{11}, R^2 = Me
b; R^1 = *n*-Bu, R^2 = Me
c; R^1 = Ph, R^2 = Me

a; R = H
b; R = Me

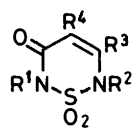


(**4**) (**5**) (**6**)

a; R^1 = Ph, R^2 = Me
b; R^1 = R^2 = Me
c; R^1 = *n*-Bu, R^2 = Me
d; R^1 = *n*-Bu, R^2 = NH_2

a; R^1 = C_6H_{11}, R^2 = Me, R^3 = H
b; R^1 = *n*-Bu, R^2 = Me, R^3 = H
c; R^1 = Ph, R^2 = Me, R^3 = H
d; R^1 = Ph, R^2 = Me, R^3 = Br

a; R = H
b; R = Me



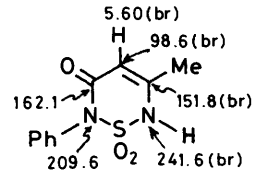
(**7**) **a**; R^1 = Ph, R^2 = R^3 = Me, R^4 = H
b; R^1 = R^2 = R^3 = Me, R^4 = H
c; R^1 = R^3 = Me, R^2 = Ph, R^4 = H
d; R^1 = R^3 = Me, R^2 = Ph, R^4 = Br

Results and Discussion

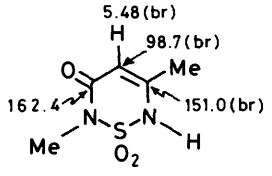
2,5-*Disubstituted* 2H-1,2,6-*Thiadiazin*-3(4H)-*one* 1,1-*Dioxides* (**4**).—Compounds (**4a**—**d**) have been studied together with two 2,5,6-trisubstituted derivatives [(**7a**) and (**7b**)] useful as models of NH-tautomers

Polar aprotic solvents: dimethyl sulphoxide (*DMSO*). The ^{15}N n.m.r. spectra of compounds (**4a**) and (**4c**) show two signals in the range δ 210—245 p.p.m. characteristic of pyrrole-type nitrogens of the 1,2,6-thiadiazine 1,1-dioxides.[3] This fact provides clear evidence of the predominance of the NH-tautomer C in this solvent. The signals belonging to N-6 appear broader than those belonging to N-2; this fact is discussed later in connection with the ^{13}C n.m.r. results.

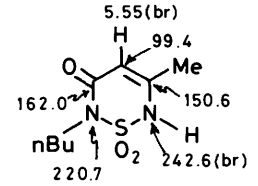
In non-tautomeric thiadiazine 1,1-dioxides[3] the Δδ effect of the methylation on the directly bonded nitrogen gives a value of +16 p.p.m. If this correction is applied to the N-6 chemical shifts of (**4a**) (241.6 + 16 = 257.6 p.p.m.) and (**4c**) (242.6 + 16 = 258.6 p.p.m.) they almost coincide with the



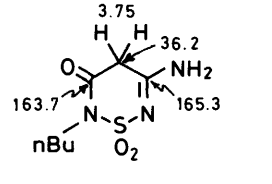
(4a)



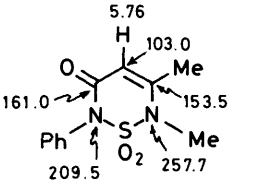
(4b)



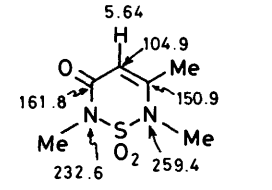
(4c)



(4d)

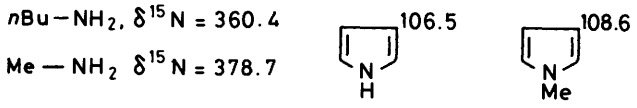


(7a)



(7b)(^{1}H,^{13}C in $CDCl_3$)

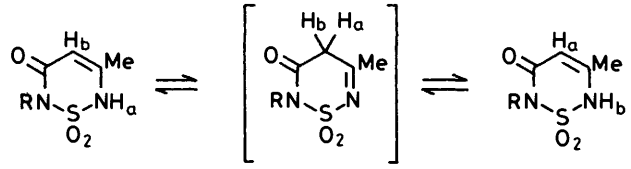
values found for (**7a**) and (**7b**). Even considering the inherent approximations of all methods based on the additivity of chemical shifts, these calculations allow us to assertain that the NH-tautomer C is present in concentrations of at least 95% in compounds (**4a**) and (**4c**). The 11.9 p.p.m. difference in the N-2 chemical shifts of compound (**4c**) (*N*-n-butyl) and (**7b**) (*N*-methyl) correspond to a β-effect.[4]



The ^{13}C chemical shifts of the compound pairs (**4a**) and (**7a**) and (**4b**) and (**7b**) agree with the conclusion that ⩾95% of the NH-tautomer exists in DMSO. The C-4 deshielding (4.4 and 6.2 p.p.m., respectively) due to *N*-methylation corresponds to enamine-type behaviour; compare, for example the chemical shifts of the pyrroles represented above.[5]

It is important to note that the signals belonging to C-4 and C-5 are broad whereas that of C-3 is narrow. Thus, a part of the molecule, comprising these two carbons plus the nitrogen N-6, is involved in a dynamic process. In order to gain some knowledge about this process, the ^{1}H n.m.r. spectra of compounds (**4a**—**c**) were recorded in [$^2H_6$]DMSO. The signals corresponding to the 4-H and (N)6-H protons are broad. When the temperature was raised from 20 up to 100 °C, these signals broadened until they became lost in the baseline (at 100 °C). The phenomenon is reversible.

A classical tautomeric process involving two or more species, one of them largely predominant, does not produce a broadening of the signals whatever the tautomeric rate. Tentatively, we assign the temperature-dependent broadening of 4-H, C-4, C-5, N-6, and 6-H to a C ⇌ C interconversion involving the CH-tautomer A present in minute quantities, through hydrogen-bonded polymers (Scheme). This process allows exchange of the N–H and C–H protons without changing the tautomeric proportions.



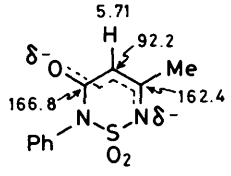
C A C

Scheme.

The effect of concentration on the behaviour of (**4a**) has been studied by ^{1}H n.m.r. spectroscopy. The spectrum has been recorded at concentrations of 0.08, 0.16, 0.32, and 1.28 M-DMSO. No new signal appears and the chemical shifts remain unchanged, the only observable effect is an increasing broadening of the 4-H signal. This result is coherent with the mechanism proposed.

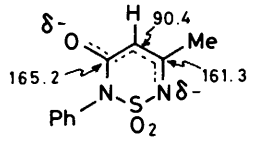
When the 5-methyl group of (**4c**) is replaced by an amino group (**4d**) the equilibrium is completely shifted towards the CH-tautomer A; both the ^{1}H and the ^{13}C spectra show the characteristic signal of the CH_2 group at 3.75(s) and 36.2(t) p.p.m., respectively.

Basic aprotic solvents: pyridine. The ^{1}H n.m.r. spectrum of (**4a**) recorded in pyridine is only compatible with the OH- and NH-tautomers. However, the ^{13}C chemical shifts are quite different from those found in DMSO. A possibility that has been considered (and excluded) in the case of the pyrazolones is ionization due to the basicity of the solvent.[6] Such a possibility is much more probable in the case of the thiadiazin-3(4*H*)-one 1,1-dioxides (pK_a about 4 or 5 compared with pyrazolones pK_a 7—9).[1,7] We have recorded the ^{13}C n.m.r. spectrum of (**4a**) in [$^2H_6$]DMSO after addition of a large excess of sodium hydride; without doubt the spectrum of (**4a**) in pyridine is similar to that of the anion D.



(4a)

([$^2H_5$]pyridine)

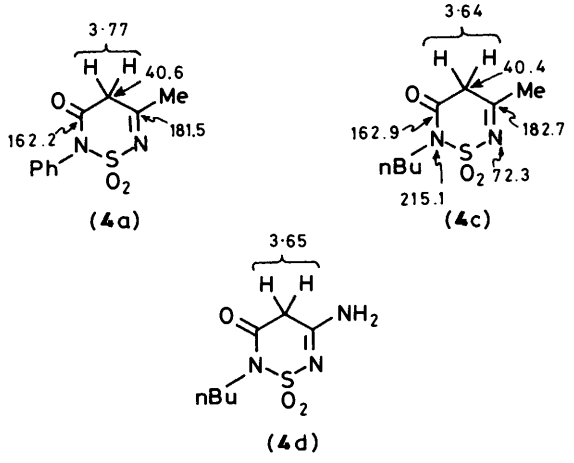


Anion D

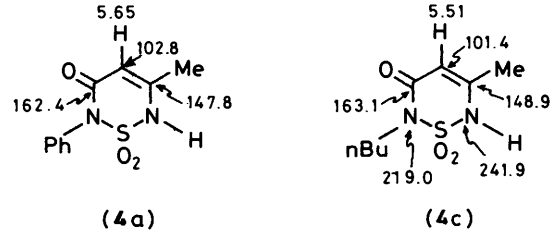
([$^2H_6$]DMSO—NaH)

Non-polar solvents: chloroform. In this solvent the CH-tautomer A is observable for both (**4a**) and (**4c**). Its proportion can be determined from the ^{1}H n.m.r. spectra; 55% for (**4a**) and 30% for (**4c**). The 'H n.m.r. spectrum of compound (**4d**) shows only signals corresponding to the CH-tautomer A (its insolubility in $CDCl_3$ prevents the recording of the ^{13}C n.m.r. spectrum).

The assignment of ^{13}C chemical shifts is based on the coupled spectra of (**4c**); the signal at δ182.7 p.p.m. appears as a triplet of quadruplets (^2J 5.8 Hz) due to couplings with the methylene and the methyl protons. The ^{15}N n.m.r. spectrum of (**4a**) cannot be recorded due to low solubility of this compound in $CDCl_3$, whereas the ^{15}N spectrum of (**4c**) is characteristic of a CH-tautomer A with two very different kinds of nitrogen atoms.



The other tautomer present in $CDCl_3$ in the case of (**4a**) and (**4c**) is the NH-tautomer C as can be easily deduced from the chemical shifts.



These are very similar to those recorded in DMSO, particularly the nitrogen chemical shifts of (**4c**). However, there are some differences concerning the C-4 and C-5 chemical shifts, *ca.* +4 p.p.m. in the case of C-4 for (**4a**) and about +2 p.p.m. for C-4 of (**4c**), which are probably related to the non-intervention of the mechanism depicted in the Scheme (all signals are narrow in $CDCl_3$). In the ^{13}C coupled spectra of (**4c**) the signal at δ148.9 p.p.m. appears as a doublet (^2J 6.2 Hz) of quadruplets (^2J 3.1 Hz).

Protic solvents: methanol. The u.v. data for compounds (**4**) and (**7**) are gathered in Table 1 and are consistent with the predominance of the NH-tautomer C except in the case of compound (**4d**). We have recorded the ^{13}C n.m.r. spectrum of the latter compound in deuteriomethanol; only the signals corresponding to the CH-tautomer A are present: 165.6 (C-3) 36.8 (C-4), and 167.1 (C-5) p.p.m.

Comparison between 1,3-*disubstituted* 1H-*pyrazol*-5(4H)-*ones* (**1**) *and* 2,5-*disubstituted* 2H-1,2,6-*thiadiazin*-3(4H)-*one* 1,1-*dioxides* (**4**). When the non-aromatic CH-tautomer A is largely favoured, as in the amino-substituted compounds (**d**), there is no difference between both classes of heterocycles (Table 2). For compounds *N*-phenyl (**a**) and *N*-alkyl (**b**) (methyl) or (**c**) (n-butyl), the main difference is the absence of the OH-tautomer B in the thiadiazinones. Unexpectedly, the NH-tautomer C is more stable for the thiadiazinones than for the pyrazolones with regard to the CH-tautomer A. Thus, the stability of the NH-tautomer C is not due to its 'aromatic' character in the pyrazolones, but to the conjugated fragment N–C=C–C=O present in both structures. The decrease in stability of the tautomer A going from R^1 = Ph to R^1 = alkyl is common to both the pyrazolones (DMSO) and the thiadiazinones ($CDCl_3$).

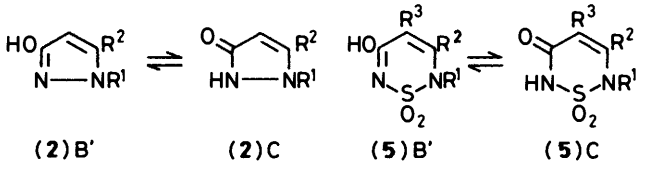
2,3,4-*Trisubstituted* 2H-1,2,6-*thiadiazin*-5-*ol* 1,1-*Dioxides* (**5**).—Both in the case of pyrazol-3-ols (**2**) and thiadiazin-5-ols (**5**) only two tautomers are possible; the OH B′, and the NH C.

Table 1. U.v. data (methanol) of 2,5-disubstituted 2*H*-1,2,6-thiadiazin-3(4*H*)-one 1,1-dioxides

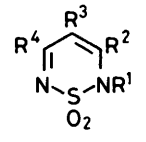
Compound	$\lambda_{max.}$(nm)	ε(dm^3 mol^{-1} cm^{-1})
(**4a**)	261	6 500
	293sh	
(**4b**)	262	7 000
	295sh	
(**4c**)	258	7 300
(**4d**)	277	2 100
(**7a**)	268	9 800
(**7b**)	264	10 600

Table 2. Tautomeric equilibria of pyrazol-5(4*H*)-ones and 2*H*-1,2,6-thiadiazin-3(4*H*)-one 1,1-dioxides

Compound	DMSO	Pyridine	$CDCl_3$	MeOH
Pyrazolones				
(**1a**)	20% CH	OH: High	100% CH	10% CH
	OH: High	NH: Low		30% CH
	NH: Low			60% NH
(**1b**)	8% CH		100% CH	5—10% CH
	80% OH			15—20% OH
	12% NH			70—75% NH
(**1d**)	100% CH		100% CH	100% CH
Thiadiazinones				
(**4a**)	100% NH	Anion	55% CH	NH: High
			45% NH	OH: Low
(**4c**)	100% NH		30% CH	NH: High
			70% NH	OH: Low
(**4d**)	100% CH		100% CH	100% CH



Compounds (**5a**—**d**) have been synthesized and studied; the three *N*-methylated derivatives (**7b**—**d**) and three *O*-methylated derivatives (**8b**—**d**) have been used as model compounds.



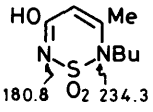
(**8**) a ; $R^1 = R^2 = R^3 = H$, R^4 = MeO
b ; $R^1 = R^2$ = Me, $R^3 = H$, R^4 = MeO
c ; R^1 = Ph, R^2 = Me, $R^3 = H$, R^4 = MeO
d ; R^1 = Ph, R^2 = Me, R^3 = Br, R^4 = MeO

Polar aprotic solvents: DMSO. Proton chemical shifts cannot be used to describe the B′ ⇌ C equilibrium. In contrast, the ^{13}C values gathered in Table 3 show that the equilibrium is largely shifted towards the OH-tautomer B′ in this solvent [compare pairs (**5**) and (**8**) against pairs (**5**) and (**7**)]. The only significant difference concerns C-4 of the bromo-derivatives (**5d**) and (**8d**) (2.8 p.p.m.) which probably reflects some steric hindrance between the methoxy and the bromo substituents.

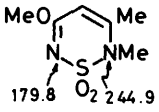
Table 3. ^1H and ^{13}C Chemical shifts of substituted 1,2,6-thiadiazine 1,1-dioxides (solvent: [$^2H_6$]DMSO)

Compound	^1H N.m.r. 4-H	^{13}C N.m.r. C-5	C-4	C-3
(5a)	5.49	168.5	93.0	160.5
(5b)	5.53	168.6	92.3	158.5
(5c)	5.75	168.4	92.2	157.9
(5d)	—[b]	164.7	89.6	155.1
(7b)[a]	5.64	161.8	104.6	150.9
(7c)	5.98	161.4	105.4	151.0
(7d)	—[b]	158.2	104.9	145.9
(8b)[a]	5.46	167.0	92.1	157.4
(8c)	5.90	168.1	91.7	158.1
(8d)	—[b]	163.4	86.8	156.3

[a] $CDCl_3$. [b] 4-Bromo-derivatives.



(5b)



(8b)

^{15}N N.m.r. spectroscopy conclusively confirms the existence of the OH-tautomer B′ in DMSO.

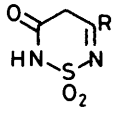
Basic aprotic solvents: pyridine. The ^{13}C spectrum of (**5a**) in pyridine shows that signals at δ 170.7 (C-5), 91.0 (C-4), and 157.6 (C-3) p.p.m. are quite similar to those found in DMSO (Table 3). Thus, the same OH-tautomer B′ is present in both solvents, although in pyridine the OH group is probably ionized to some extent, but not so much as in the case of (**4a**), since the spectrum in [$^2H_6$]DMSO–NaH is quite different, δ180.6 (C-5), 100.1 (C-4), and 148.6 (C-3) p.p.m.

Non-polar solvents: chloroform. The ^{13}C n.m.r. spectrum of (**5b**) in chloroform was difficult to record due to its low solubility. The chemical shifts 168.3 (C-5), 94.9 (C-4), and 157.9 (C-3) p.p.m. are almost identical to those observed in DMSO (Table 3) and leave no doubt of the OH-structure in chloroform.

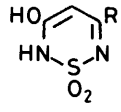
Protic solvents: methanol. The data gathered in Table 4 show that the *N*-methyl isomers (**7**) absorb at 265 nm (ε ~ 11 000) whereas the *O*-methyl isomers (**8**) absorb at 295 nm (ε ~ 6 500). Thus, *N*-alkyl derivatives (**5a**) and (**5b**) are in the OH form and the *N*-phenyl derivative (**5c**) exists as a mixture of both tautomers B′ and C.

Comparison between 1,5-disubstituted 1H-pyrazol-3-ols (**2**) *and 2,3,4-trisubstituted 1,2,6-thiadiazin-5-ol 1,1-dioxides* (**5**). For compounds (**2**)[1] and (**5**) the only tautomer present in the three solvents studied is the OH-tautomer B′.

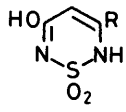
5-Substituted 2H-1,2,6-Thiadiazin-3(6H)-one 1,1-Dioxides (**6**).—Owing to their low solubility the compounds (**6a, b**) have been studied only in DMSO (^1H, ^{13}C, ^{15}N n.m.r.) and in methanol (u.v.). Four tautomers are possible, (**6**) A, (**6**) B, (**6**) B′, and (**6**) C, as in the case of corresponding pyrazolones.[1]



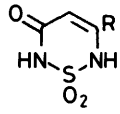
(6)A



(6)B



(6)B′

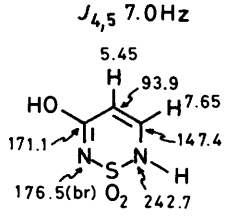


(6)C

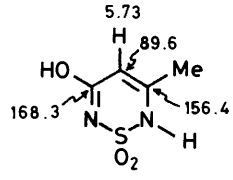
Table 4. U.v. data (methanol) of substituted 1,2,6-thiadiazine 1,1-dioxides

Compound	$\lambda_{max.}$(nm)	ε(dm^3 mol^{-1} cm^{-1})
(5a)	290	7 200
(5b)	295	7 750
(5c)	261	7 500
	293	5 250
(7b)	264	10 600
(7c)	266	11 700
(8b)	294	6 150
(8c)	296	6 800

Polar aprotic solvents: DMSO. The ^1H n.m.r. spectra exclude the (**6**) A tautomer. Of the three other tautomers, the ^{13}C chemical shifts of compound (**6b**) are much closer to those of (**8b**) (model of tautomer B′) than to those of (**7b**) (Table 3, model of tautomer C). Finally, the ^{15}N chemical shifts of (**6a**) are very similar to those of (**8b**) and (**5b**) but different to those of (**7b**). In conclusion, 5-substituted 2H-1,2,6-thiadiazin-3(6*H*)-one 1,1-dioxides (**6**) exist in DMSO as the 3-OH tautomer (**6**) B′.



(6a)



(6b)

Protic solvents: methanol. Compound (**6a**) absorbs at 282 nm (ε = 4 200) and compound (**6b**) at 278 nm (ε = 5 300). This absorption is intermediate between that of compound (**8b**) (294 nm) and that of compound (**7b**) (264 nm), and it is not possible to conclude about the predominant tautomer, B′ or C, present in methanol. Since these compounds are very insoluble in methanol, the ^{13}C n.m.r. spectra cannot be recorded in order to determine the position of the B′ ⇌ C equilibrium in this solvent.

Comparison between 5-substituted 1H-pyrazol-3(2H)-ones (**3**) *and 5-substituted 2H-1,2,6-thiadiazin-3(6H)-one 1,1-dioxides* (**6**). There is a total agreement between both classes of compound: 5-substituted pyrazolones[1] exist in DMSO as 3-hydroxy tautomers (**3**) B′ and in methanol as mixtures of tautomers (**3**) B′ and (**3**) C.

Conclusions

In the case of pyrazolones, depending on the substituents and on the solvent, the four tautomers A, B, B′, and C play an important role. In contrast, the thiadiazinone 1,1-dioxide OH-tautomer B is never present.

The effect of the SO_2 group is two-fold: (i) it interrupts the aromatic conjugation (tautomers B and B′) (ii) it causes the pyridine-type nitrogens to become less basic and the pyrrole-type like nitrogens to become more acidic. On the whole the tautomer stability in thiadiazinone 1,1-dioxides follows the order: B′ > C > A > B.

B′ is much less acidic than B [(**5a**) is un-ionized or ionized to only a very small extent in pyridine when compared with (**4a**)]

and it is well known[1] that the more acidic tautomers are less stable. A similar situation is observed for 3(5)-alkoxypyrazoles; the 3-alkoxy tautomer [corresponding to (**6**) B′] is always more stable than the 5-alkoxypyrazole [corresponding to (**6**) B].[1] Intuitively, it is easy to understand that groups such as OH, OR, and NH_2 ($+M$ and $-I$ effects) confer greater stability upon the structure α to the imino nitrogen than α to the amino nitrogen.

Experimental

^1H N.m.r. spectra were recorded at 200 MHz on a Bruker AM-200 spectrometer. ^{13}C N.m.r. spectra were recorded at 20.15 MHz on a Bruker WP-80 or at 75 MHz on a Varian XL 300 spectrometers. Chemical shifts are reported as δ values (p.p.m.) relative to Me_4Si as internal standard. The natural-abundance ^{15}N n.m.r. spectra were obtained at 30.41 MHz on a Varian XL 300 spectrometer, using 1.0M solutions in a mixture of DMSO–[$^2H_6$]DMSO (10%) to provide the locking signal or in $CDCl_3$ and contained in 10 mm o.d. tubes. The ^{15}N n.m.r. spectra were recorded under the following conditions: 14 KHz spectral width, 32 K data table, 70° pulse angle, 8 s pulse repetition, and broad-band ^1H decoupler on only during the acquisition time to suppress the n.O.e. Chemical shifts were determined with respect to external neat nitromethane in the σ scale (shielding being a positive increment). U.v. spectra were recorded with a Perkin-Elmer 402 spectrophotometer.

The thiadiazin-3-one derivatives were prepared by reported procedures: (**4a**), (**5a**), (**5c**), (**7a**), (**7c**) and (**8c**),[8] (**4b**), (**7b**), and (**8b**),[9] (**4c**) and (**5b**),[10] (**6a**),[11] and (**6b**).[12] The synthesis of (**4d**), (**5d**), (**7d**), and (**8d**) will be published elsewere. ^1H and ^{13}C N.m.r. spectra in DMSO of reported compounds are described in the same publications except for ^{13}C n.m.r. data of (**6a**),[3] (**6b**);[9] (**4c**) 162.0 (C-3), 99.4 (C-4), 150.6 (C-5), 19.4 (Me-5), 40.1 (C-7), 30.8 (C-8), 19.7 (C-9), 13.6 (C-10), and **5b**: 168.6 (C-5), 92.3 (C-4), 158.5 (C-3), 19.8 (Me-3), 42.5 (C-7), 30.8 (C-8), 19.5 (C-9), and 13.5 (C-10).

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