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A ^{15}N NMR Study of the Tautomeric Equilibria of Some 5-Substituted Tetrazoles

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^{15}N NMR shielding data are presented for some 5-tetrazolones and some 5-tetrazolethiones. CNDO/S-SOS nitrogen shielding calculations are also performed for these compounds. The results obtained show that the compounds studied exist almost entirely in the oxo and thioxo forms, rather than the hydroxy or mercapto forms respectively, in DMSO solution.

We have previously reported some ^{15}N NMR data for both unsubstituted tetrazole[1] and some 5-mercapto-substituted[2] tetrazoles. In the case of some 5-hydroxytetrazoles electronic spectral data have been reported. Prototropic tautomerism is of some considerable interest in the field of azole chemistry.[4] The results reported indicate that the tetrazoles studied exist almost entirely in the thioxo and oxo forms rather than the mercapto and hydroxy forms respectively.

Our earlier studies have revealed that prototropic tautomerism of both unsubstituted and 5-(methylthio)-tetrazoles give rise to a predominance of the structure with a proton attached to N-1. In both cases this structure is reported to be present to the extent of about 85%.[1,2]

We now propose to investigate the possibility of prototropic tautomerism in 5-mercaptotetrazole and 1-methyl-5-hydroxytetrazole.

Results and Discussion

The results of a ^{15}N NMR investigation of 5-tetrazolone, 5-tetrazolethione and some related compounds are given in Table 1 together with the results of some CNDO/S-SOS nitrogen shielding calculations. The latter are reported on the absolute scale, whereas the experimental ^{15}N shieldings are given with respect to that of nitromethane. Consequently a one-to-one correspondence between these two sets of shielding data is not to be anticipated. However, for a given compound the calculated relative order of nitrogen shielding data is sufficiently reliable to permit their use for signal assignment purposes.[1]

In addition to the CNDO/S-SOS shielding results the nitrogen shielding assignments presented in Table 1 are obtained from a knowledge that pyrrole-type nitrogen atoms are highly shielded[5] with respect to pyridine-type nitrogen atoms. Bonding to another nitrogen atom produces a deshielding of the first nitrogen and bonding to two other nitrogens gives rise to a further nitrogen deshielding.[5]

Compounds **2** and **3** are studied as models for compound **1** which, in principle may exist as a tautomeric mixture of structures A, B, C, and D in DMSO. The structures of compounds **2** and **3** are known from literature data,[2] preparation and the assignments given in Table 1 of their ^{15}N NMR spectra are consistent with this.

The experimental data given in Table 1 for compound **1** is very similar to that of compound **3** which, of neccesity, exists as structure A. Therefore structure A is clearly the predominant one for compound **1**. However, we had initially anticipated that compound **1** would have existed mainly, if not entirely, in form B. Our reason for supposing this is by comparison with compound **2** which is demonstrated to consist of form B.[1] A possible explanation of our observation of form A for compound **1** is that solvent interactions lead to a preference of form A over form B.

Turning now to a consideration of the nitrogen shielding data for compounds **4** and **5**. In principle compound **4** may exist as a mixture of tautomers. In order to investigate this possibility compound **5** has been studied as a model compound.

The nature of the tautomeric equilibria in which compound **4** may be involved is as follows:

From a comparison of the results given in Table 1 for compounds **4** and **5** it is apparent that compound **4** exists in DMSO predominantly as form E. Any amount

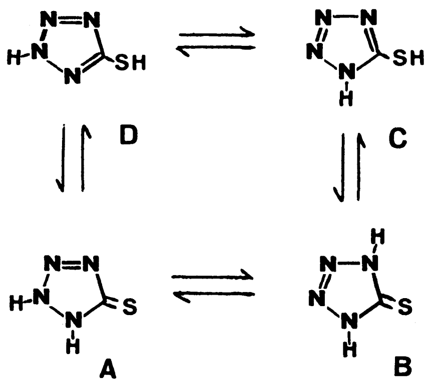


Fig. 1.

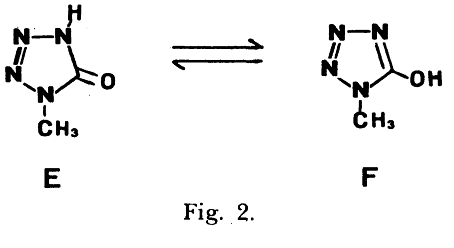
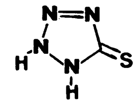
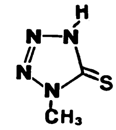
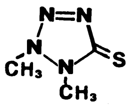
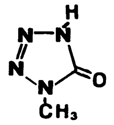
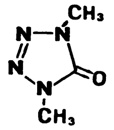
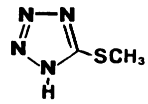
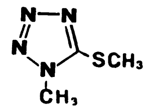
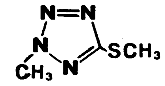


Fig. 2.

Table 1. ^{15}N NMR Shielding Data[a] for Some 5-Tetrazolones and Some 5-Tetrazolethiones Obtained by Experiment and Calculation by the CNDO/S-SOS Procedure

Number	Compound[a]	Nitrogen atom	Experimental results in DMSO	Theoretical results[b,c]
1		N-1	82.2	38.2
		N-2	70.4	35.1
		N-3	−3.9	−52.1
		N-4	50.4	−38.5
2		N-1	151.9	70.1
		N-2	25.4	−32.4
		N-3	17.4	−33.1
		N-4	145.7	64.2
3		N-1	97.3	61.4
		N-2	70.9	45.2
		N-3	−4.5	−56.1
		N-4	47.7	−39.7
4		N-1	193.1	68.2
		N-2	43.2	−33.7
		N-3	33.6	−34.6
		N-4	187.7	62.4
5		N-1 N-4	193.2	70.7
		N-2 N-3	39.1	−41.0
6		N-1 N-4	100.5	55.3 −10.2
		N-2 N-3	4.5	−26.1 −36.3
7		N-1	158.1	70.1
		N-2	7.1	−27.1
		N-3	−11.1	−36.9
		N-4	55.6	−9.8
8		N-1	81.6	−27.6
		N-2	101.4	42.4
		N-3	−2.3	−50.9
		N-4	53.4	−35.3

a) All shielding data are reported in ppm. The experimental results relate to external nitromethane as standard; a possible increment corresponds to a shielding increase. b) The structures given are predominant in DMSO solutions and the theoretical shielding results relate to these structures. c) The theoretical results relate to absolute shieldings.

of form F present is predicted to be less than 5%. In the case of compound **4** the assignment of the N-2 and N-3 signals is consistent both with the deshielding influence of a β-effect and with the predictions of the CNDO/S-SOS shielding data. The relative assignments of the N-1 and N-4 signals are based on a comparison of the assignment of compound **2**, the shielding results observed for compound **5** and those calculated by the CNDO/S-SOS procedure for compound **4**.

In conclusion we observe that ^{15}N NMR spectroscopy is a very satisfactory procedure for investigating tautomeric equilibria of some 5-substituted tetrazoles. Additionaly, we note that CNDO/S-SOS parametrized shielding calculations are suitable for estimating the relative shieldings of the nitrogen atoms in the tetrazole ring.

Experimental

Compounds **1**,[6] **4**,[7] and **5**[7] were prepared by previously published procedures, while compound **2** was obtained commercially. Compound **3** was prepared by methylating the sodium salt of 2-methyl-5-mercaptotetrazole with dimethyl sulfate in equimolar amounts in methanol as solvent according to procedure published elsewhere.[1] The purity of all compounds employed was varified by means of ^{1}H and ^{13}C NMR measurements.

The ^{15}N NMR spectra were obtained on a Bruker WH 400 spectrometer using 10 mm sample tubes for 0.5 M (1 M=1 mol dm^{-3}) solutions at ambient temperatures. Nitromethane was used as an external standard. Typical operating conditions employed a delay of about 2s between pulses, a pulse angle of about 70° and an aquisition time of 0.5s. Gated decoupling was used to suppress possible NOE effects.

The CNDO/S-SOS shielding calculations were performed on the CDC 7600 system of the University of London using a modified version of QCPE 174. The details of the calculations are presented elsewhere.[8] Standards geometries were used in the calculations.[9]

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