Preparation, Mass and NMR Spectra of Some Isotopic Thiazoles

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The syntheses of [4-D]-, [2-^{13}C]- and a mixture of [4-^{13}C]- and [5-^{13}C]thiazole have been carried out. The mass spectra of [2-D]-, [4-D]-, [5-D]- and [2-^{13}C]thiazole confirm the break-down pattern of thiazole, previously suggested by other authors on the basis of mass spectra of derivatives of thiazole. NMR spectra of [^{15}N]-, [2-^{13}C]-, [4-^{13}C]-, [5-^{13}C]-, 2-bromo-[2-^{13}C]-, 2-amino-[4-^{13}C]- and 2-amino-[5-^{13}C]-thiazole gave (H−H)-, (^{15}N−H)- and (^{13}C−H)-, direct and long range, coupling constants. These coupling constants were also determined by a CNDO/2-calculation. Finally, calculated and experimental line widths of [^{14}N]- and [^{15}N]thiazole are compared.

The microwave spectrum of thiazole has been analysed,[1] and the substitution structure according to the Kraitchman-Costain method [2,3] has been obtained.[4] This method demands the recording and analysis of the microwave spectra of all the monoisotopically substituted thiazoles. The syntheses of all these compounds (except [^{34}S]thiazole of which the natural abundance of 4 % is sufficient for the recording of the microwave spectrum) has been described by Braun and Metzger,[5] who kindly provided us with samples of [^{15}N]-, [2-D]-, and [5-D]thiazole. Braun and Metzger also provided us with samples of [2-^{13}C]- and [4-D]thiazole, but these samples did not contain detectable amounts of the compounds when their microwave spectra were recorded. We have therefore synthesized these compounds and also a mixture of the remaining two isotopic thiazoles, [4-^{13}C]- and [5-^{13}C]thiazole.
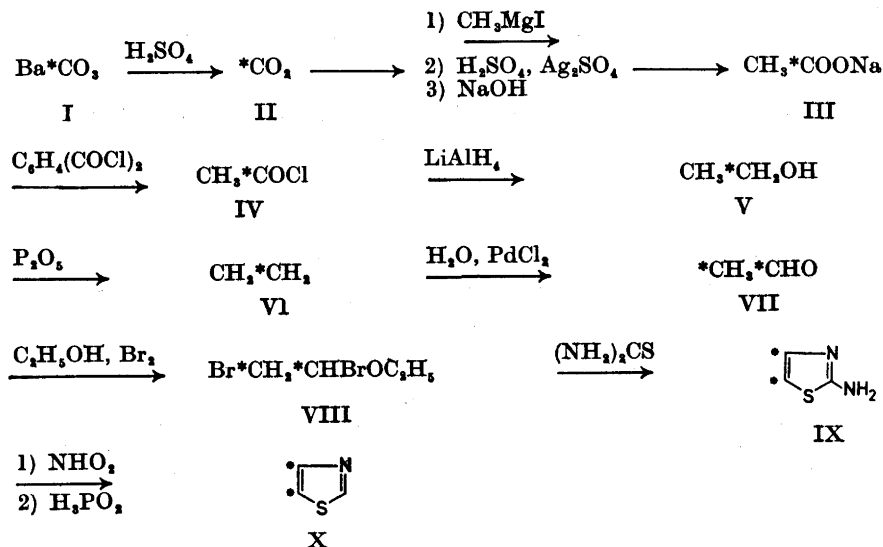
NMR spectra were obtained for all the isotopic species of thiazole as well as two intermediate products, 2-bromo-[2-^{13}C]thiazole and 2-amino-[4-^{13}C]-thiazole, 2-amino-[5-^{13}C]thiazole. Analysis of the spectra yielded coupling constants of the types J_{HH}, J_{HC}, and J_{HN}. Based on the structure determined from microwave spectra the coupling constants have been calculated

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using the CNDO/2 procedure, and these values have been compared to the experimental results. The presence of [^{15}N]- and [^{14}N]thiazole as a mixture has made a detailed study of line width possible. Calculated values and results obtained from ^{14}N NMR data have been compared to experiment.

Synthesis of [4 -^{13}C] - and [5 -^{13}C]thiazole

[4-^{13}C]- and [5-^{13}C]thiazole were synthesized according to the scheme:

$$Ba*CO_3 \xrightarrow{H_2SO_4} *CO_2 \longrightarrow \begin{array}{c} 1)\ CH_3MgI \\ \xrightarrow{\hspace{2cm}} \\ 2)\ H_2SO_4,\ Ag_2SO_4 \\ 3)\ NaOH \end{array} \longrightarrow CH_3*COONa$$

$$\text{I} \qquad\qquad \text{II} \qquad\qquad\qquad\qquad\qquad\qquad \text{III}$$

$$\xrightarrow{C_6H_4(COCl)_2} CH_3*COCl \xrightarrow{LiAlH_4} CH_3*CH_2OH$$

$$\text{IV} \qquad\qquad\qquad\qquad \text{V}$$

$$\xrightarrow{P_2O_5} CH_2*CH_2 \xrightarrow{H_2O,\ PdCl_2} *CH_3*CHO$$

$$\text{VI} \qquad\qquad\qquad\qquad \text{VII}$$

$$\xrightarrow{C_2H_5OH,\ Br_2} Br*CH_2*CHBrOC_2H_5 \xrightarrow{(NH_2)_2CS} \text{IX}$$

$$\text{VIII}$$

$$\xrightarrow[2)\ H_3PO_2]{1)\ NHO_2} \text{X}$$

The asterisk (*) indicates the position that is enriched in ^{13}C. If the molecular formula contains two asterisks, *either* one *or* the other of the two positions is enriched, and the sample will contain a mixture of the two. Starting with BaCO$_3$, enriched to ~50 % one ended up with a mixture of [4-^{13}C]- and [5-^{13}C]thiazole each enriched to 25 % which was ample for the analysis of the microwave spectra.

The synthesis of (V) has been described previously.[6,7] The yield of 2.22 g of (V) from 12.4 g of (I) was 76 %.

Our method of synthesis of (X) from (V) differed in two ways from that described by Braun and Metzger.[5] Firstly, (V) was not oxidized directly to the corresponding acetaldehyde, but the production of (VI) was inserted, thus ensuring that the two wanted isotopic thiazoles were both produced eventually. Secondly, the ring formation with (NH$_2$)$_2$CS was performed by using (VIII) rather than the bromoacetaldehyde suggested by Braun and Metzger. (VIII) was found to be much easier to handle (acetaldehyde has a tendency for polymerisation on bromination), and the yield was just as good.

1.189 g (25.3 mmol) of (V) reacted with 12.5 g P$_2$O$_5$ according to Bak *et al.*[8] produced 0.6 g (21 mmol) of (VI).

Following a method of Smidt *et al.*,[9,10] 17.8 g CuCl$_2$·2H$_2$O, 5.4 g (CH$_3$COO)$_2$Cu·H$_2$O and 0.150 PdCl$_2$, dispersed in 25 ml H$_2$O, was stirred vigorously at room-temperature in an atmosphere of 0.6 g (21 mmol) of (VI) for 48 h. The acetaldehyde formed was isolated by distillation on the vacuum line at −78°C. The fraction with vapour pressure > 2 mmHg consisted of 0.73 g (16.6 mmol) of (VII). An infrared spectrum of the sample showed it to contain very little ethylene and no water.

The synthesis of unlabelled (VIII) from unlabelled (VII) is described by Seifert.[11] 0.73 g (16.6 mmol) of (VII) was dissolved in 0.78 g of absolute ethanol and 2.72 g Br_2 was added dropwise at $-5°C$. The reaction was vigorous and effective cooling was necessary. A two-phase system was obtained. (VIII) was rather unstable. It was therefore without isolation immediately used for the synthesis of (IX).

Vogel has performed this reaction with the corresponding dichloroether.[12] Both phases mentioned were added dropwise to a boiling solution of 1.26 g thiourea in 7 ml of water. After cooling, conc. NaOH was added until the solution was basic, and (IX) was isolated by continuous extraction with ether. Yield 1.238 g (12.38 mmol).

The synthesis of (X) was carried out by diazotation and reduction by hypophosphorous acid. This was similar to the procedure followed by Braun and Metzger.[5]

The final amount of (X) constituted 0.238 g. This was equivalent to an over-all yield of 10 % (X) from (I).

Synthesis of [2-¹³C]thiazole
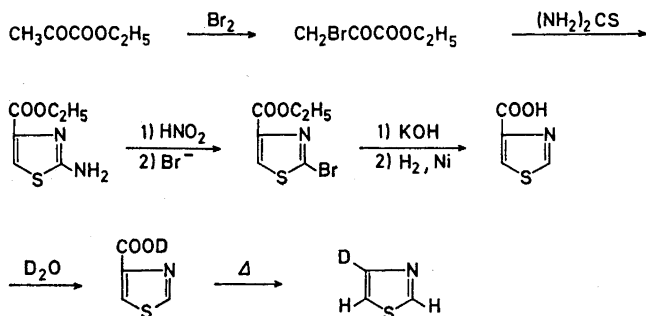
For [2-¹³C]thiazole the sequence of reactions was:
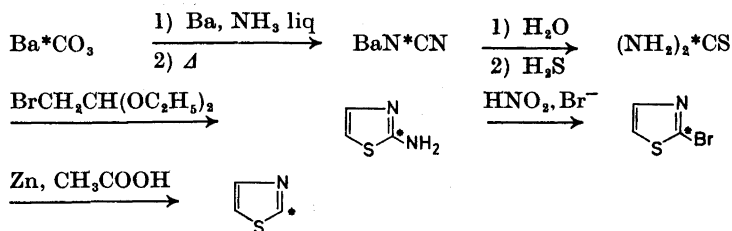
This synthesis follows essentially the same lines as that described by Braun and Metzger.[5]

Starting from 6.0 g of $BaCO_3$ enriched to 55 % in ¹³C, the yield of [2-¹³C]thiazole was 0.043 g. This is equivalent to an overall yield of 1.5 %.

Synthesis of [4-D]thiazole

[4-D]thiazole was synthesized according to the scheme:

The synthesis of thiazole-4-carboxylic acid from pyruvic acid ethyl ester has been described in detail by Erlenmeyer and Morel,[13] and their procedure was followed closely, except for the third step where the diazotation and reduction were carried out according to Sandmeyer instead of by the Gattermann reaction suggested.

Thiazole-4-carboxylic acid was recrystallised from D_2O, until the broad $-COOH$ absorption band at $2700 - 3300$ cm^{-1} had disappeared from the infrared spectrum. The total yield of thiazole-4-[D]carboxylic acid from pyruvic acid was 9.7 %.

[*4-D*]*thiazole*. To the best of our knowledge the decarboxylation of thiazole-4-carboxylic acid has not been described in detail in the literature, though Schenkel and Schenkel [14] have observed that decarboxylation occurs at 184°C using quinoline as a solvent, whereas if no solvent is used, complete destruction takes place. We therefore used the following procedure.

1.00 g (8.5 mmol) thiazole-4-[D]carboxylic acid was dissolved in 5 ml of quinoline in a 300 ml sample tube and 0.3 g of cupric oxide was added. The tube was evacuated, sealed off and heated at $180 - 184$°C for 16 h. After cooling, the tube was opened and the formed thiazole was distilled off on the vacuum line. Yield: 0.350 g (4.2 mmol) ~50 %.

At this stage it was not to be known whether any [4-D]thiazole had been formed. Because of the great lability of the transition state formed during the decarboxylation it was possible that the D-atom would migrate to the 2 -or the 5-position of the molecule, thus producing a dominating amount of [2-D]- or [5-D]thiazole. Or, because of the excess of quinoline present, the D-atoms might react with these molecules so that in fact no deutero thiazole was produced at all.

The mass spectrum of the product was recorded. The intensity ratio of mass peak 85 (parent) and mass peak 86 (essentially monodeutero thiazoles) was 2:1. Some deutero thiazole had therefore been formed.

The NMR spectrum of the sample looked very similar to the spectrum of the parent compound described in Ref. 15. However, the ratio of the integrated peak heights was not 1:1:1, but rather 90:80:100 for the 2-, 4-, and 5-protons, respectively.

These two analytical results showed that the sample contained thiazole, [4-D]-, [2-D]-, and [5-D]thiazole in the ratio 70:20:10:~0. A comparison of identical rotational transitions of the four compounds in the microwave spectrum of the sample showed this ratio to be 70:20:5:5, in good agreement with the analytical results.

MASS SPECTRA OF ISOTOPIC THIAZOLES

The mass spectra of thiazole and a number of derivatives have been recorded by Clarke *et al.*[16] They found that the spectra were dominated by the molecular ions and by fragments formed by cleavage of the 1,2- and 3,4-bonds, with charge retention by the sulfur-containing portion. For thiazole itself they then postulate that this portion will form a thiirene ion-radical by cyclisation. This ring will break down further by elimination of a CH-fragment.

Mass spectra of suitable isotopic thiazoles gave an affirmative check on this break-down pattern. The spectra of [2-D]-, [2-^{13}C]-, and [4-D]thiazole showed that the elimination of HCN does indeed take place by cleavage of the 1,2- and 3,4-bonds and not by cleavage of the 2,3- and 4,5-bonds.

If formation of the thiirene ring takes place before the elimination of CH, there would be the same statistical chance for the original C(4)H(4)- and C(5)H(5)-fragment to be abandoned, whereas if no ring formation occurs one would expect that it was primarily the C(4)H(4)-radical that was eliminated. The mass spectra of [4-D]- and [5-D]thiazole showed that ring formation does take place.

NMR SPECTRA

In the following section the NMR spectra of a number of substituted thiazoles are discussed. The thiazole samples were prepared using CS_2 as solvent and adding TMS as internal reference. The samples were degassed

and sealed in vacuum. 2-Bromo-[2-^{13}C]thiazole was dissolved in $CDCl_3$ + TMS and 2-aminothiazoles dissolved in CD_3OD + TMS forming a saturated solution.

Table 1. Experimental and calculated, proton-proton coupling constants (Hz) in isotopic substituted thiazoles.

Species	$J_{H(2)H(4)}$	$J_{H(2)H(5)}$	$J_{H(4)H(5)}$
[^{15}N]^a	0.60 ± 0.05	1.96 ± 0.01	3.13 ± 0.05
[2-^{13}C]^b	–	1.9 ± 0.1	3.1 ± 0.1
2-Br-[2-^{13}C]^a	–	–	3.40 ± 0.05
[4-^{13}C]^b	0.60 ± 0.10	–	–
2-NH$_2$-[4-^{13}C]^a	–	–	3.81 ± 0.10
[5-^{13}C]^b	0.60 ± 0.10	–	3.15 ± 0.10
2-NH$_2$-[5-^{13}C]^a	–	–	3.27 ± 0.10
Calculated	1.80	1.34	2.04

^{a} $T = 32°C$.
^{b} $T = -30°C$.

The spectra of 2-bromo-[2-^{13}C]thiazole were recorded at a Varian A60 spectrometer at 32°C. All other spectra were recorded at a Varian HA-100 spectrometer in the frequency sweep mode. Relative signs for the coupling constants were found by tickling experiments. Analysis of the spectra was performed using the LAOCOON II program [17] iterating on all lines observed. The final data are listed in Tables 1 and 2.

[^{15}N]*thiazole.* A sample containing 10 mg [^{15}N]thiazole enriched to 30 % was prepared, dissolving it in 300 μl CS_2.

In Fig. 1 the spectrum of [^{15}N]thiazole is reproduced. It is evident from the details inserted that due to the presence of [^{15}N]thiazole each line from the parent molecule is flanked by a considerably sharper doublet.
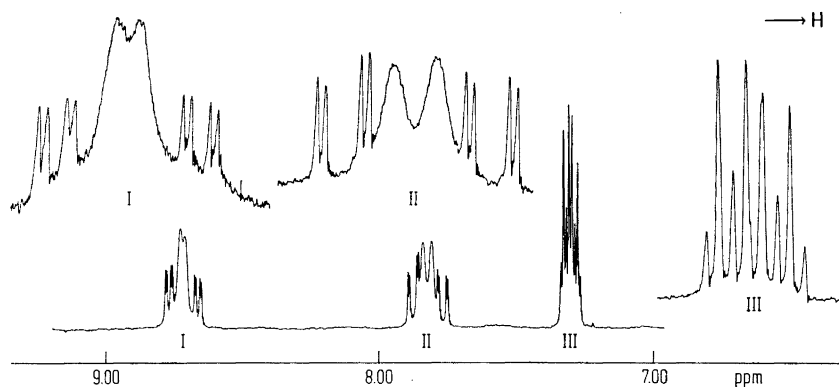

Fig. 1. ^{1}H NMR spectrum of [^{15}N]- and [^{14}N]thiazole. I, II, III corresponding to signals due to H(2), H(4), and H(5), respectively.

Table 2. Coupling constants (Hz) in isotopically substituted thiazoles between ^{13}C and H or ^{14}N and H. The heading of the column indicates the substitution in thiazole.

Species	$[2\text{-}^{13}C]^b$	$2\text{-Br-}[2\text{-}^{13}C]^a$	$[4\text{-}^{13}C]^b$	$2\text{-NH}_2\text{-}[4\text{-}^{13}C]^a$	$[5\text{-}^{13}C]^b$	$2\text{-NH}_2\text{-}[5\text{-}^{13}C]^a$	$[^{15}N]$
$^1J^{13}CH$	211.1 ± 0.5	—	186.5 ± 0.4	184.0 ± 0.1	189.1 ± 0.2	191.2 ± 0.1	$J^{15}NH(2)$　-10.56
$^2J^{13}CH$	—	—	7.2 ± 0.2	6.10 ± 0.1	16.4 ± 0.4	14.26 ± 0.1	$J^{15}NH(4)$　-10.6
$^3J^{13}CH$	H(4): 15.5 ± 0.2	19.5 ± 0.3	14.9 ± 0.4	—	<3.6	—	$J^{15}NH(5)$　-1.97
	H(5): 6.2 ± 0.5	8.5 ± 0.3					

^{a} $T = 32°C$.
^{b} $T = -30°C$.

From the ^{15}N compound the coupling constants between ring protons could be determined with greater accuracy than in the parent molecule. The results listed in Table 1 yield an RMS error of 0.05 Hz. The results obtained for $J_{H(2)H(5)}$ and $J_{H(4)H(5)}$ were close to the results obtained earlier.[15,18,19] $J_{H(2)H(4)}$ cannot be observed in the parent molecule at room temperature, but Kintzinger and Lehn [20] found a value of 0.6 Hz at $-37°C$. This is identical with our result. Tickling experiments and selective decoupling [21] showed the three ring HH coupling constants to be of the same sign (positive). The $J_{^{15}NH}$ coupling constants were determined all to have the same sign (negative). The numerical values are given in Table 2.

[2-^{13}C]thiazole. The sample consisted of 5 μl of enriched thiazole dissolved under the same conditions as given above.

The spectrum yielded the [13]CH long range coupling constants, both being of the same sign (positive). Improved spectral resolution was obtained by cooling the sample from 32°C to $-30°C$. The coupling constants reported are obtained from the low temperature spectra.

[4-^{13}C] and [5-^{13}C]thiazole. The sample consisted of 25 μl of enriched material dissolved as described above.

From the spectrum, accurate data could be obtained for ^1J and ^2J [13]CH coupling constants. The long range coupling constants to H(2) were difficult to establish accurately due to the line shape for H(2) lines which were broadened by the neighbouring ^{14}N atom. From tickling experiments it was determined that the signs of all [13]CH coupling constants were positive for [4-^{13}C] as well as [5-^{13}C]thiazole. Low temperature spectra resulted in better resolution, permitting a better estimate of line positions. In the case of [4-^{13}C]thiazole one of the H(4)[13]C satellites overlapped with the H(2) signals. Since the chemical shift differences are temperature dependent the H(4) satellite could be easily identified comparing spectra at various temperature. Data reported for the [4-^{13}C]- and [5-^{13}C]thiazole were obtained from spectra at $-30°C$.

2-Bromo-[2-^{13}C]thiazole. The sample was prepared from 25 μl of enriched 2-bromothiazole dissolved in $CDCl_3$ using TMS as standard.

In this molecule very large [13]CH long range couplings were observed (see Table 2). These values are in agreement with the expectation that electronegative substitution on ^{13}C leads to increased [13]CH coupling constants.

2-Amino-[4-^{13}C]- and 2-amino-[5-^{13}C]thiazole. The spectra showed that the [13]CH long range coupling constants are positive but smaller than the values found in thiazole.

CALCULATION OF THEORETICAL COUPLING CONSTANTS

On the basis of the microwave determination of the structure of thiazole it was possible to carry out a CNDO/2 calculation of the coupling constants in the molecule. The calculation applies an sp-basis set of valence orbitals, and includes the Coulomb integrals between occupied and vacant molecular orbitals. This method has been found [22,23] to represent the major contribution from configuration interaction. The calculated results are listed in Tables 1 and 3.

Table 3. CNDO/2 calculation of coupling constants (Hz) in isotopic substituted thiazole.

Species	[2-¹³C]		[4-¹³C]	[5-¹³C]	[¹⁵N]	
$^1J_{13CH}$		81.27	73.38	78.20		
$^2J_{13CH}$		—	2.45	4.95	$J_{15NH(2)}$	− 4.65
					$J_{15NH(4)}$	− 4.48
$^3J_{13CH}$	H(4):	6.75			$J_{15NH(5)}$	− 1.12
	H(5):	4.94	7.73	2.63		

The HH coupling constants were all calculated to be positive and $J_{H(4)H(5)}$ was correctly calculated to be the largest. The coupling between H(2) and H(5) was in reasonable agreement with experiment, while H(2)H(4) was calculated three times as large as the value actually found. This is a general feature, found in several other substituted heteroaromatics studied.[24]

¹⁵N coupling constants were all calculated to be negative as expected from experiments. The calculated values were too small by a factor of 2 to 3, but the relative magnitudes of the coupling constants were correctly reproduced.

The $^1J_{13CH}$ coupling constants have been reported before,[25] and our experimental results were in close agreement with these. The calculated coupling constants were correctly predicted to be positive, but they were too small. This fact has been established by Pople *et al.*[26] in a recent survey. The relative magnitude reflects correctly the experimental data.

LINE WIDTH IN [¹⁵N]- AND [¹⁴N]THIAZOLE

The quadrupole moment of the ¹⁴N nucleus is responsible for the pronounced broadening of ¹H signals observed for H(2) and H(4).[20] The ¹⁴N quadrupole coupling tensor has been determined from microwave gas spectra.[4] It is nearly of axial symmetry and as a good approximation we may take e^2qQ/h to be − 4.41 MHz. In the present investigation thiazole was used as a dilute solution in CS_2 and it is a good approximation to take over this value for the liquid phase. The correlation time τ_q can in the classical approximation be obtained [27] as

$$\tau_q = \frac{4\pi\eta a^3}{3kT} \tag{1}$$

Here, $\eta_{32} \cong \eta_{32}(CS_2) = 3.3 \times 10^{-5}$ poise. $a = 3.5$ Å. The molecular radius a was calculated as the mean distance of hydrogen atoms from the centre of gravity plus van der Waal radius of hydrogen (1.2 Å). From the data above it was possible to calculate the quadrupolar relaxation time T_q for ¹⁴N using the equation

$$\frac{1}{T_q} = \frac{3}{8}\left(\frac{e^2qQ}{h}\right)^2 \tau_q \tag{2}$$

The equation yielded the value $1/T_q = 96.1$ Hz.

The line shape of the proton signals in thiazole can be obtained from an expression given by Pople [28]

$$I(x) \propto \frac{45 + u^2(5x^2 + 1)}{225x^2 + u^2(34x^4 - 2x^2 + 4) + u^4(x^6 - 2x^4 + x^2)} \qquad (3)$$

here $x = \Delta v / J_{^{14}NH}$; $u = 10\pi T_q J_{^{14}NH}$
Δv being the distance from the centre of the signal.

From the observed coupling constants $J_{^{14}NH(i)}$ we obtained $J_{^{14}NH(i)}$ from the relation

$$J_{^{14}NH(i)} = -0.7129 \times J_{^{14}NH(i)} \qquad (4)$$

yielding $J_{^{14}NH(2)} = 7.528$ Hz; $J_{^{14}NH(4)} = 7.564$ Hz; $J_{^{14}NH(5)} = 1.404$ Hz.

Kintzinger and Lehn have derived an expression for the half line width on the basis of eqn. (3) where $x(\tfrac{1}{2})$ is found from the equation

$$(1530u^2 - 56u^4 - 2u^6) \, x(\tfrac{1}{2})^4 + (10125 + 135u^2 + 3u^4 + u^6) \, x(\tfrac{1}{2})^2$$
$$- 180u^2 - 4u^4 = 0 \qquad (5)$$

and the full line width at half height Δ is

$$\Delta = 2x(\tfrac{1}{2}) \, J_{^{14}NH} \qquad (6)$$

Using the data derived above we obtained the Δ values given in Table 4 as (I).

Kintzinger and Lehn determined experimentally the half line width in the ^{14}N resonance spectrum of thiazole $\Delta_N = 155$ Hz. This allows the independent calculation of u

$$u = \frac{10 \times J_{^{14}NH}}{\Delta_N} \qquad (7)$$

From these data a line width Δ is calculated and given in Table 4 as (II).

The experimental full line width at half height Δ has been measured for $[^{15}N]$- and $[^{14}N]$thiazole in the same sample. The difference in line width Δ is due to quadrupole interaction and should be compared to the calculated values.

Table 4. Calculated and experimental line width (Hz) for protons in thiazole.

	$\Delta H(2)$	$\Delta H(4)$	$\Delta H(5)$
Calculated Δ (I)	4.8	4.9	0.17
Calculated Δ (II)	0.96	0.98	0.03
Experimental ^{14}N	~ 1.9	~ 2.0	0.35
— ^{15}N	0.20	0.25	0.25
— Δ	1.7	1.7	0.10

It is seen from Table 4 that the values calculated on the basis of eqns. (1) − (2) resulted in line width larger than the experimentally observed. This is probably due to the approximate nature of eqn. (1). The data calculated

on basis of eqn. (7) resulted in a line width a little smaller than the observed one. Here the lack in accuracy in determination of Δ_N is the main source of error. As a result of this, Kintzinger and Lehn predicted the ^{15}NH coupling constants a little larger than the actual values $J_{^{15}NH(2)}$: 12.6 Hz, $J_{^{15}NH(4)}$: 15.12 Hz.

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Received December 15, 1970.