

# PROTON AND CARBON-13 NUCLEAR MAGNETIC RESONANCE OF SOME 4-AMINO-3-ALKYL (ARYL)-5-THIO-1,2,4- TRIAZOLINES AND THEIR DERIVATIVES

By

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*Key Words:*  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra, 1,2,4-triazoline derivatives

## ABSTRACT

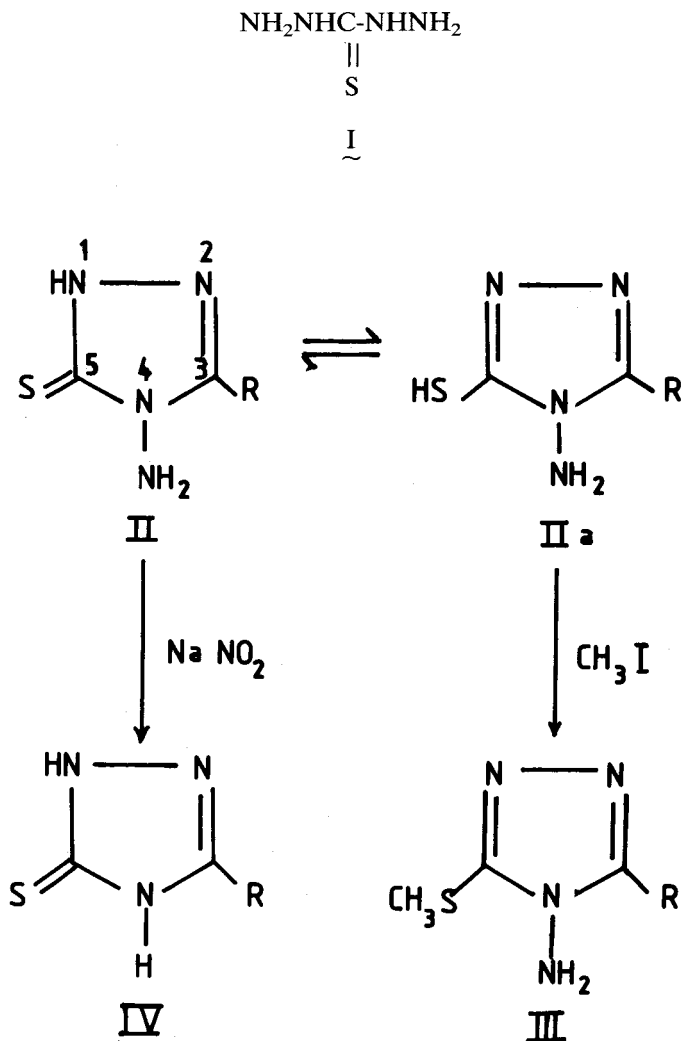
The proton and carbon-13 NMR spectra of some 4-amino-3-alkyl(aryl)-5-thio-1,2,4-triazolines, some 3-alkyl-5-thio-1,2,4-triazolines and some 4-amino-3-aryl-5-thio-1,2,4-triazoles were measured in DMSO- $d_6$  as solvent. The chemical shift for each proton and carbon in these compounds were assigned. The  $^1\text{H}$ , chemical shift of N-H protons of the thioamide group and the  $^{13}\text{C}$  chemical shift of C(3) in the triazolines were found to be sensitive to the substituent R (alkyl or aryl) at C(3), and correlated to Taft substituent constant  $\sigma^*$ . The deprotonation constants  $p^{\text{Ka}}$  of the 4-amino-1,2,4-triazolines were correlated linearly with the proton chemical shift,  $\delta$ , of the thioamide N-H protons.

## INTRODUCTION

Thiocarbohydrazide, I, has many analytical (Duval and Xyong, 1956; Duval and Loc, 1956) biological (Margoliash *et al.*, 1960; Donovan *et al.*, 1950; Cline and Pearce, 1966) and industrial (Thurmaier, 1965; Clayton and Marraccini, 1966; Riedel, 1965) applications and it is a very useful starting material for synthesis of many heterocyclic compounds (Kurzer and Wilkinson, 1970). Among them 4-amino-3-alkyl(aryl)-5-thio-1,2,4-triazolines, II, (R=H,  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$ ,  $\text{CF}_3$ ,  $\text{C}_6\text{H}_5$ ,  $p\text{-Cl-C}_6\text{H}_4$  and  $p\text{-CH}_3\text{O-C}_6\text{H}_4$ ). The reaction of II with  $\text{CH}_3\text{I}$  affords the corresponding 1,2,4-triazole derivatives III.

These heterocyclic compounds possess the thiocarbohydrazide skeleton N-N-C(S)-N-N fixed in cis-trans configuration (Braibante *et al.*, 1969; Braibanti *et al.*, 1971). Treatment of II with acidified  $\text{NaNO}_2$  solution resulted in formation of the

deaminated form IV (Kurzer and Wilkinson, 1970).



In continuation of our studies on the acid-base and ligation properties (El-Toukhy *et al.*, 1990) and corrosion inhibition of steel and aluminium in acid and alkaline media (Abd-El Nabey *et al.*, 1986) of II, we present here the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra of II, III and IV and correlate their chemical shifts to their deprotonation constants, p<sup>K</sup>a (El-Toukhy *et al.*, 1990) and Taft substituent constants, σ\* (Taft, 1956).

## EXPERIMENTAL

Thiocarbohydrazide,  $\text{I}$ , was prepared by the hydrazinolysis of  $\text{NH}_2\text{NHCSSNH}_3\text{NH}_2$  according to the method of Audrieth (Audrieth *et al.*, 1954).

4-amino-3-alkyl-5-thio-1,2,4-triazolines,  $\text{II}$  ( $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$  and  $\text{CF}_3$ ) were prepared from thiocarbohydrazide as previously described by Beyer and Kroger (Beyer *et al.*, 1960). 3-Alkyl-5-mercapto-1,2,4-triazolines  $\text{IV}$  ( $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5$  and  $\text{C}_3\text{H}_7$ ) were obtained by deamination of the corresponding  $\text{II}$ , performed by reaction of an acidified solution of  $\text{II}$  with 0.5N  $\text{NaNO}_2$  (Beyer, *et al.*, 1960). The isolated crude triazolines were crystallized from aqueous ethanol.

4-amino-3-aryl-5-thio-1,2,4-triazolines ( $\text{II}$ ,  $\text{R} = \text{C}_6\text{H}_5, \text{p-Cl-C}_6\text{H}_4, \text{p-CH}_3\text{O-C}_6\text{H}_4$ ) were prepared by the method suggested by Hoggarth, (Hoggarth, 1952). Reaction of these aryl triazoline derivatives with  $\text{CH}_3\text{I}$  resulted in the formation of the corresponding 4-amino-3-aryl-5-methylthio-1,2,4-triazoles  $\text{III}$  ( $\text{R} = \text{C}_6\text{H}_5, \text{p-Cl-C}_6\text{H}_4$  and  $\text{pCH}_3\text{O-C}_6\text{H}_4$ ) (Hoggarth, 1952). The purity of all these compounds was checked by TLC and melting point determination.

**Physical measurements:**

$^1\text{H-NMR}$  spectra were recorded using a JOEL-FX-200 spectrometer operating at 199.5MHz. Samples were dissolved in  $\text{DMSO-d}_6$  and tetramethylsilane (TMS) was used as an internal standard. The  $^{13}\text{C-NMR}$  spectra of the samples were recorded by using JEOL JNM-FX-200 spectrometer operating at 50.10 MHz in the pulsed F.T. mode under broad band decoupling conditions. 25-30 mg of the samples were dissolved in 1 ml of  $\text{DMSO-d}_6$  and placed in 5 mm tubes.  $\text{DMSO-d}_6$  was used as a "lock" solvent and chemical shifts were measured relative to TMS, ( $\delta = 0$  ppm).

## RESULTS AND DISCUSSION

Similar to other heterocyclic compounds containing thioamide group  $\text{NH-C=S}$  (De Fillippo and Preti, 1970; DeFillippo *et al.*, 1971; Colombini and Preti, 1975; Begtrup, 1972; Sinha *et al.*, 1977), the triazolines,  $\text{II}$  can exist either in the thione,  $\text{II}$ , or the thiol  $\text{IIa}$  forms. In solid state, both  $\text{II}$  and  $\text{IV}$  exist in the thione form as evident from their infrared spectra (De Fillippo and Preti, 1970; DeFillippo *et al.*, 1977; Colombini and Preti, 1975; Begtrup, 1972; Sinha *et al.*, 1977). In solution, however, both thione and thiol forms are in equilibrium and the deprotonation constants  $\text{p}^{\text{K}}_{\text{a}}$  of the thiol tautomer,  $\text{IIa}$ , were reported (El-Toukhy *et al.*, 1990). The  $\text{p}^{\text{K}}_{\text{a}}$  values for the deprotonation reaction  $\text{II} \rightleftharpoons \text{IIa}$ , suggested that the substituent  $\text{R}$  in  $\text{II}$  series greatly influences the acidity of the thio tautomer as evident from the linear correlation between  $\text{p}^{\text{K}}_{\text{a}}$  and Taft substituent constant  $\sigma^*$ .

Since chemical shifts in many classes of compounds are known to be subject to steric (through space) effects associated with atoms or groups which are geometrically close to a particular carbon or hydrogen atoms although remote from it topologically. However, chemical shifts are also determined by inductive (through bonds) effects and it is therefore important to establish at an early stage the extent to which these electronic effects may be transmitted from one part of the molecule to another. It is with this aspect that the present paper is primarily concerned.

The <sup>1</sup>H-NMR spectra for the 1,2,4-triazoline derivatives, II, (R= H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, C<sub>3</sub>H<sub>7</sub>, CF<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>, p-Cl-C<sub>6</sub>H<sub>4</sub> and pCH<sub>3</sub>O-C<sub>6</sub>H<sub>4</sub>) and IV (R= H, CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> and C<sub>3</sub>H<sub>7</sub>) are collected in Table 1, together with those of some S-CH<sub>3</sub> triazole

**Table 1**  
<sup>1</sup>H-NMR data for II, III and IV in DMSO-d<sup>6</sup>.  
 Chemical shifts are in PPM from TMS

| R   | δ (PPM)         |                     |     |                |                 |                  |                  |                |
|---|-----------------|---------------------|-----|----------------|-----------------|------------------|------------------|----------------|
|   | CH <sub>3</sub> | CH <sub>2</sub>     | CH  | NH             | NH <sub>2</sub> | OCH <sub>3</sub> | SCH <sub>3</sub> | Aromatic-H     |
| <u>II</u> , H   | —               | —                   | 8.4 | 13.72          | 5.6             |                  |                  |                |
| <u>II</u> , CH <sub>3</sub>                                   | 2.1             |                     |     | 13.50          | 5.5             |                  |                  |                |
| <u>II</u> , C <sub>2</sub> H <sub>5</sub>                     | 1.2(t)          | 2.6(q)              |     | 13.46          | 5.5             |                  |                  |                |
| <u>II</u> , C <sub>3</sub> H <sub>7</sub>                     | 0.8(t)          | 1.6(Sx),<br>2.5(t)  |     | 13.44          | 5.4             |                  |                  |                |
| <u>II</u> , CF <sub>3</sub>                                   |                 |                     |     | 14.5           | 5.8             |                  |                  |                |
| <u>II</u> , C <sub>6</sub> H <sub>5</sub>                     |                 |                     |     | 13.8           | 5.7             |                  |                  | 7.5 - 7.9(m)   |
| <u>II</u> , p-Cl-C <sub>6</sub> H <sub>4</sub>                |                 |                     |     | 13.9           | 5.7             |                  |                  | 7.5(d), 8.0(d) |
| <u>II</u> , p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>  |                 |                     |     | 13.7           | 5.7             | 3.75             |                  | 7.0(d), 7.9(d) |
| <u>III</u> , C <sub>6</sub> H <sub>5</sub>                    |                 |                     |     |                | 5.95            |                  | 2.52             | 7.1 - 7.9(m)   |
| <u>III</u> , p-Cl-C <sub>6</sub> H <sub>4</sub>               |                 |                     |     |                | 5.95            |                  | 2.53             | 7.2(d), 8.0(d) |
| <u>III</u> , p-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> |                 |                     |     |                | 5.90            | 3.75             | 2.50             | 7.0(d), 7.9(d) |
| <u>IV</u> , H   |                 |                     | 8.2 | 13.25<br>13.50 |                 |                  |                  |                |
| <u>IV</u> , CH <sub>3</sub>                                   | 2.1             |                     |     | 13.0(b)        |                 |                  |                  |                |
| <u>IV</u> , C <sub>2</sub> H <sub>5</sub>                     | 1.1(t)          | 2.5(q)              |     | 12.2(b)        |                 |                  |                  |                |
| <u>IV</u> , C <sub>3</sub> H <sub>7</sub>                     | 0.85(t)         | 1.6(Sx),<br>2.55(t) |     | 11.4(b)        |                 |                  |                  |                |

b = broad;            d = doublet;            t = triplet;  
 m = multiplet;      q = quartet;            Sx = sextet.

derivatives, III, ( $R = C_6H_5$ ,  $p\text{-Cl-C}_6H_4$  and  $p\text{-CH}_3O\text{-C}_6H_4$ ). Both types of II and IV triazolines show a very down field signal due to N-H protons of the thioamide group which disappeared on deuteration. Lack of such this signal on the  $^1H\text{-NMR}$  spectra of III together with the presence of the S-CH<sub>3</sub> signal at ca.2.5 ppm confirm the triazole structure III. The chemical shift,  $\delta$ , for the N-H proton in compounds II, and IV, Table 1, is sensitive to the substituent R. This is evident from the linear correlation between the chemical shift  $\delta$  and  $pK_a$  (El-Toukhy *et al.*, 1990) of II series as well as Taft substituent constant  $\sigma^*$  (Taft, 1956), Figures 1 and 2.

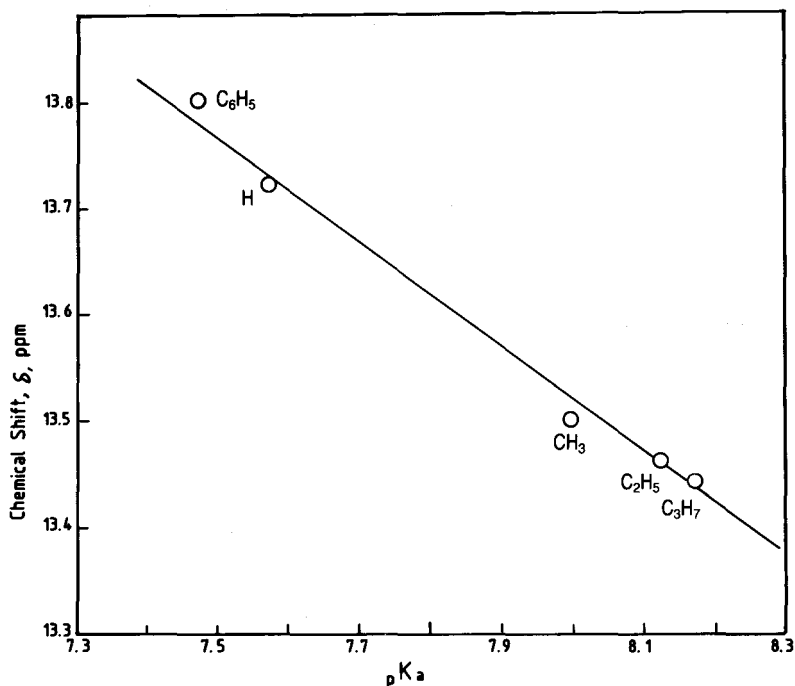


Fig. 1: Relationship between the thioamide N-H proton chemical shift,  $\delta$ , and the deprotonation constants  $pK_a$  of II.

Thus electron donating groups in II,  $R = CH_3$ ,  $C_2H_5$ ,  $C_3H_7$ , (hyperconjugation) or II,  $R = p\text{CH}_3O\text{-C}_6H_4$ , increase the  $pK_a$  values and cause upfield shift for N-H proton relative to the unsubstituted compound II, ( $R = H$ ). Withdrawing electron density from the pyrazoline ring by electron withdrawing groups (II,  $R = CF_3$  or  $p\text{-Cl-C}_6H_4$ ) would tend to decrease the  $pK_a$  values of these derivatives and cause down field shift for the N-H proton.

Although the chemical shift of N-H protons in the deaminated triazolines IV are sensitive to the substituent R and suffer from upfield shift in methyl, ethyl and

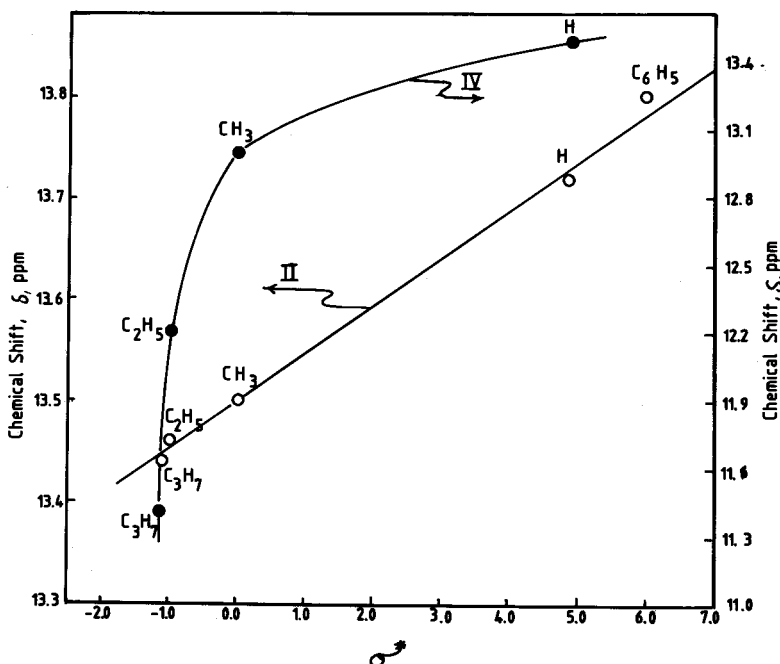


Fig. 2: Relationship between the thioamide N-H proton chemical shift,  $\delta$ , of II, O, and IV, ●, and Taft polar substituents constants ( $\sigma^*$ ).

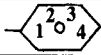
n-propyl derivatives relative to the compound IV ( $R=H$ ), the chemical shift  $\delta$  is not linear with Taft substituent constant  $\delta$ , Figure 1. The presence of two N-H centers separated by  $C=S$  in IV is tentatively proposed for the broadening of the N-H signal and the non-linearity with  $\sigma^*$ .

It is of interest to note that the chemical shift of the thioamide N-H proton for the 4-amino thiazolines II is larger than the corresponding deaminated derivatives, IV (see Table 1). This suggests that the 4-aminotriazoline derivatives II are more acidic than the corresponding deaminated derivatives IV.

The signal at  $\delta$  5.4-5.9 ppm in the  $^1H$ -NMR spectra of II and III, Table 1, can be assigned to the 4-amino protons,  $NH_2$ , which also disappeared on deuteration. Its chemical shift is essentially constant and independent of the rest of the molecule.

The  $^{13}C$  NMR spectra of the studied compounds II, III and IV at 200  $MHz$  are readily assigned. Figure 3, shows the  $^{13}C$  spectra of some substituted triazoline and triazole compounds while a complete list of  $^{13}C$  chemical shift data and assignments for the studied compounds appears in Table 2. The chemical shift,  $\delta$ , of C(3) in II and IV is very sensitive to the substituent R and it increases going from the

**Table 2**  
 $^{13}\text{C}$  NMR data for II, III and IV in DMSO- $d_6$ .  
 Chemical Shifts are in PPM from TMS.

| R  | $\delta$ (PPM)   |       |                 |                 |                   |   |                   |                   |
|--|------------------|-------|-----------------|-----------------|-------------------|---|-------------------|-------------------|
|  | C-R              | C-S   | CH <sub>2</sub> | CH <sub>3</sub> | CF <sub>3</sub>   |  | -OCH <sub>3</sub> | -SCH <sub>3</sub> |
| <u>II</u> , H  | 143              | 166   |                 |                 |                   |   |                   |                   |
| <u>II</u> , CH <sub>3</sub>                                    | 150.5            | 166   |                 | 10              |                   |   |                   |                   |
| <u>II</u> , C <sub>2</sub> H <sub>5</sub>                      | 153              | 166   | 18              | 10              |                   |   |                   |                   |
| <u>II</u> , C <sub>3</sub> H <sub>7</sub>                      | 152.5            | 166.5 | 19<br>26        | 13              |                   |   |                   |                   |
| <u>II</u> , CF <sub>3</sub>                                    | 140(q)<br>(J=53) | 170   |                 |                 | 117(q)<br>(J=226) |   |                   |                   |
| <u>II</u> , C <sub>6</sub> H <sub>5</sub>                      | 150              | 167.5 |                 |                 |                   | 126 (1)<br>128.5(2)<br>129 (3)<br>131 (4)   |                   |                   |
| <u>II</u> , P-Cl-C <sub>6</sub> H <sub>4</sub>                 | 149              | 168   |                 |                 |                   | 125 (1)<br>129 (2)<br>130.5(3)<br>136 (4)   |                   |                   |
| <u>II</u> , P-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub>  | 150              | 167   |                 |                 |                   | 115 (1)<br>119 (2)<br>130 (3)<br>162 (4)  | 56                |                   |
| <u>III</u> , C <sub>6</sub> H <sub>5</sub>                     | 151              | 154   |                 |                 |                   | 126 (1)<br>128 (2)<br>129 (3)<br>131 (4)  |                   | 12.9              |
| <u>III</u> , P-Cl-C <sub>6</sub> H <sub>4</sub>                | 150              | 154   |                 |                 |                   | 125.5(1)<br>129 (2)<br>130.5(3)<br>136 (4)  |                   | 13                |
| <u>III</u> , P-CH <sub>3</sub> O-C <sub>6</sub> H <sub>4</sub> | 154              | 153.8 |                 |                 |                   | 114 (1)<br>120 (2)<br>130 (3)<br>161 (4)  | 55.5              | 13                |
| <u>IV</u> , H  | 141              | 165   |                 |                 |                   |   |                   |                   |
| <u>IV</u> , CH <sub>3</sub>                                    | 150              | 167   |                 | 11              |                   |   |                   |                   |
| <u>IV</u> , C <sub>2</sub> H <sub>5</sub>                      | 153              | 167   | 18.5            | 10.5            |                   |   |                   |                   |
| <u>IV</u> , C <sub>3</sub> H <sub>7</sub>                      | 152.2            | 166.5 | 19.2<br>25.8    | 12.5            |                   |   |                   |                   |

q = quartet  
 the unit of J is H<sub>z</sub>

unsubstituted compounds,  $R=H$ , to  $R=C_2H_5$ . This downfield shift reflected the expected reduction of electron density on C(3) resulting from the increasing of  $C=N$  double bond character as the donation of electron by R increased. The linear correlation between the chemical shift,  $\delta$ , of C(3) and Taft substituent constants  $\sigma^*$ , Figure 4, are in agreement with this hypothesis. On the other hand, the upfield shift of C(3) resonance for **II**,  $R=CF_3$  appears as quartet centered at 140 ppm ( $J=53\text{Hz}$ ), (Figure 3, Table 2) indicates a build up of electronic density on the atom.

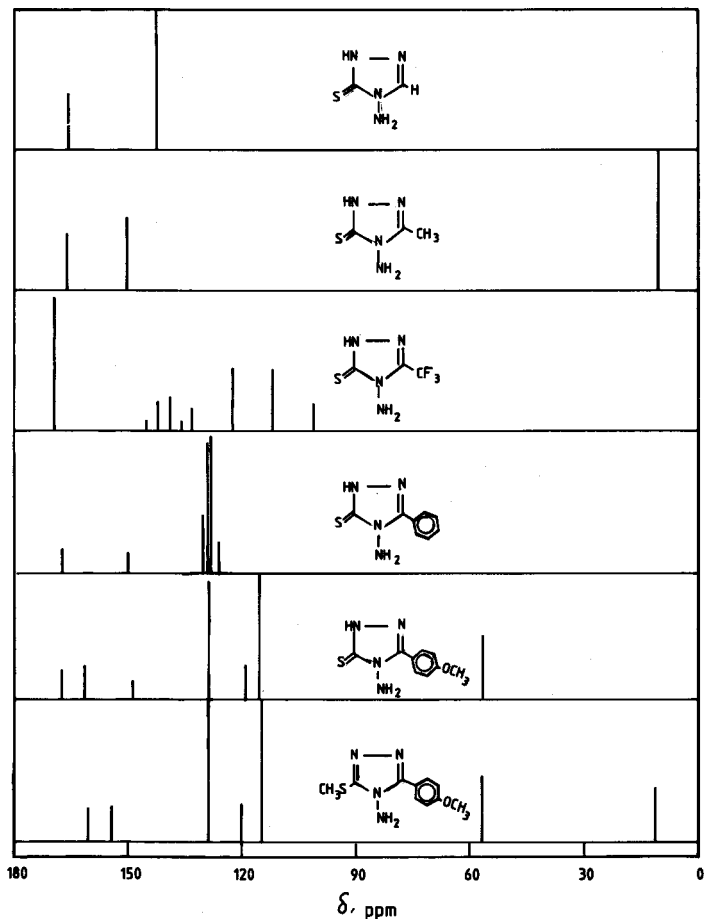


Fig. 3: 50.10 MHz  $^{13}\text{C}$ -NMR spectra of **II** ( $R = H, \text{CH}_3, \text{CF}_3, \text{C}_6\text{H}_5, \text{P-CH}_3\text{O-C}_6\text{H}_4$ ) and **III** ( $R = \text{P-CH}_3\text{O-C}_6\text{H}_4$ ) in  $\text{DMSO-d}_6$ .

The,  $\delta$ ,  $^{13}\text{C}$  value of C(5) (the  $\text{C}=\text{S}$  unit) for **II** and **IV** are fairly constant and correspond closely to the  $\delta$ ,  $^{13}\text{C}$  values of thioamido carbon containing compounds (Giuliani and Trotta, 1988; Bret, *et al.*, 1983).



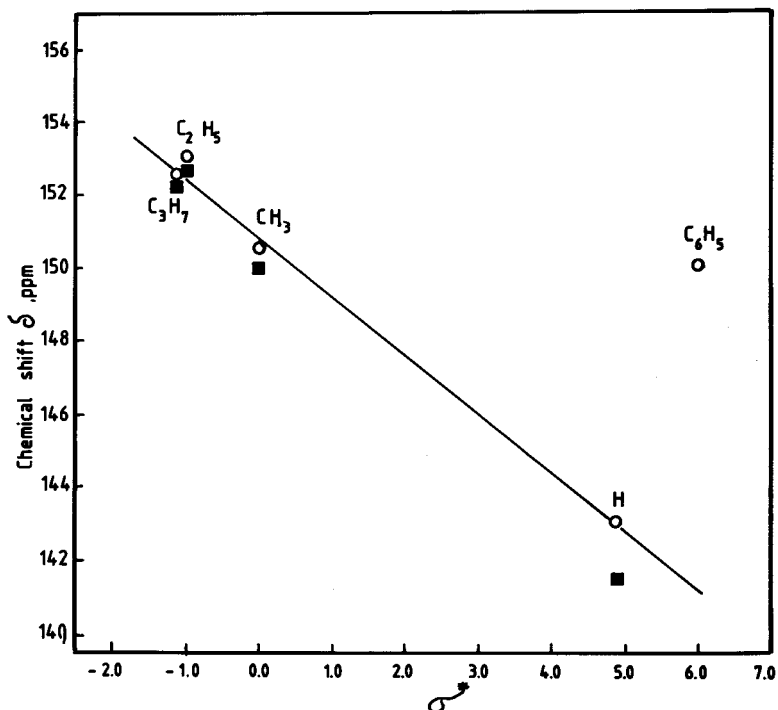


Fig. 4: Relationship between the C(3)  $^{13}C$  Chemical shift,  $\delta$ , of II, O, and IV,  $\blacksquare$ , and Taft polar substituents constants ( $\sigma^*$ ).

The resonances of C(5) show a marked upfield shift upon methylation of  $-C=S$  to  $-C-SCH_3$  (II  $\rightarrow$  III). The shielding is consistent with a lowering of the  $C=S$  bond order as already observed for the S-methyl dithiocarbamate derivatives (Manogaran and Sathyanarayana, 1983).

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طيف الرنين النووي المغناطيسي (بروتون وكربون -13) لبعض ٤ -  
أمينو - ٣ الكيل (أريل) - ٥ ثيو - ١ ، ٢ ، ٤ - تريازولين ومشتقاتهم .

أحمد الطوخي و عبدالله الكبيسي و إبراهيم قناوي

يهدف هذا البحث إلى قياس طيف الرنين النووي المغناطيسي لكل من الهيدروجين والكربون - 13 لبعض مشتقات ١ ، ٢ ، ٤ - تريازولين لمعرفة تأثير مجموعات الالكيل والاريل المختلفة والمرتبطة بذرة الكربون رقم ٣ في هذه المشتقات على الازاحة الكيميائية لكل ذرات الهيدروجين والكربون في هذه المركبات ومعرفة أي المراكز أكثر حساسية للاستبدال وقد وجد أن الهيدروجين المرتبط بمجموعة الثيواميد وذرة الكربون رقم ٣ في هذه المركبات هما أكثر المراكز تأثيراً . وقد رسمت ونوقشت العلاقة بين قيم الازاحة الكيميائية (للبروتون على مجموعة الثيواميد ( $^1\text{h.nmr}$ ) والكربون رقم ٣ ( $^{13}\text{c.nmr}$ ) مع ثوابت الاشتقاق لتأفت\*  $\sigma$  واثبتت الدراسة وجود علاقة خطية بين الازاحة الكيميائية لبروتون مجموعة الثيواميد وثوابت حامضية هذه المشتقات pka .