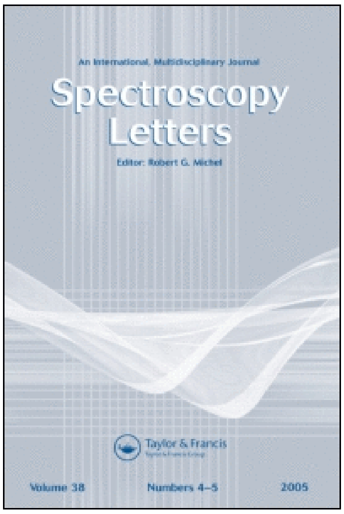

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Carbon-13 Nuclear Magnetic Resonance Spectra of Substituted-1,2,4-triazoles

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CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA OF SUBSTITUTED-1,2,4-TRIAZOLES

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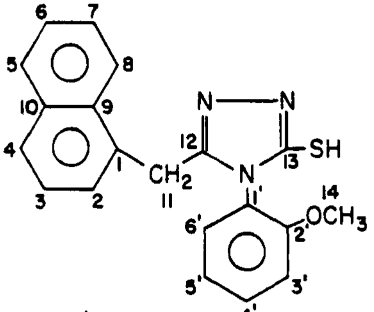
KEY WORDS: Carbon-13 NMR, proton noise decoupled, single frequency off-resonance decoupled (SFORD), chemical shifts, assignments, 5-(1-napthylmethyl)-4-(2-methoxyphenyl)-1,2,4-triazol-3-thiol and 5-(1-naphthylmethyl)-4-(2-methoxyphenyl)-1,2,4-triazol-3-yl-thioglycolic acid

ABSTRACT: The natural abundance carbon-13 nuclear magnetic resonance spectra of 5-(1-naphthylmethyl)-4-(2-methoxyphenyl)-1,2,4-triazol-3-thiol and 5-(1-naphthylmethyl)-4-(2-methoxyphenyl)-1,2,4-triazol-3-yl-thioglycolic acid were recorded using Fourier transform techniques. The chemical shift of various carbon resonances of these compounds have been assigned on the basis of the chemical shift theory, the signal multiplicity observed in the single frequency off-resonance decoupled (SFORD) spectra and comparison with the chemical shifts of model compounds.

INTRODUCTION

The compounds containing triazole moiety are getting due attention for their antiinflammatory activity[1,2]. Recently, we have reported the synthesis of 5-(1-naphthylmethyl)-4-aryl-s-triazol-3-thiol/-yl-thioglycolic acids as possible antiinflammatory agents[3]. Our continuing interest to assign the carbon-13 NMR spectra of various classes of therapeutic agents[4-10] initiated the study of two substituted triazoles[3] **1** and **2**. The assignments of the carbon resonances of **1** and **2** are of theoretical importance. Both proton noise decoupled and SFORD spectra of **1** and **2** were obtained in DMSO-d_6 as an internal lock and solvent and tetramethylsilane as a reference on a JEOL FX 60 spectrometer. The various carbon resonances of **1** and **2** have been assigned on the basis of chemical shift theory, multiplicity generated in SFORD spectrum and comparison with the corresponding carbon chemical shifts of the model compounds.



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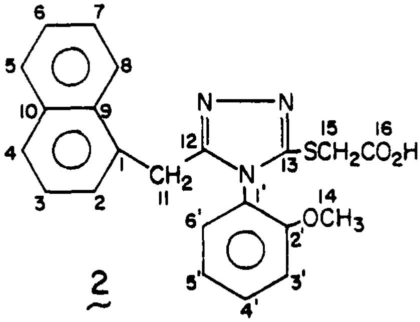

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RESULTS AND DISCUSSIONS

5-(1-Naphthylmethyl)-4-(2-methoxyphenyl)-1,2,4-triazol-3-thiol **1**

The carbon-13 NMR chemical shifts of **1** are recorded in Table I. There are seventeen signals which account for all the twenty carbon resonances of **1**. The triplet centered at 29.5 ppm and a quartet centered at 55.6 ppm are assigned to C-11 and C-14, respectively. The multiplicities for the most of the aromatic carbon resonances in the SFORD spectrum are not clear due to their very close chemical shifts in proton noise decoupled spectrum of **1**. The methoxy group attached to the benzene nucleus produces 31.4 ppm and 1.0 ppm downfield shift to the ipso and meta carbons, respectively, and 14.4 ppm and 7.7 ppm upfield shift to the ortho and para carbons, respectively[11]. The amino group attached to the benzene ring causes 18.8 ppm and 0.9 ppm downfield shifts to the ipso and meta carbons and 13.3 ppm and 9.8 ppm upfield shifts to the ortho and para carbons, respectively[11]. Considering the effect of the methoxy and the amino groups on the benzene ring attached at the 4-position of the triazole nucleus of **1**, the singlet at 151.5 ppm is assigned to C-2' and the signals observed at 128.8 and 123.6 ppm account for C-1' and C-5', respectively. The doublet centered at 120.6 ppm is attributed to the C-4' while the doublet centered at 112.6 ppm is assigned to both C-3' and C-6'. The methyl substituent present on the benzene ring produces 8.9 ppm and 0.9 ppm downfield to the ipso and ortho carbons, respectively, and 0.1 ppm and 2.9 ppm upfield shift to meta and para carbons[11], respectively. Since the naphthyl group present in **1** is affected by the methylene group at C-1, the

TABLE I

Carbon-13 NMR Chemical Shifts of 5-(1-Naphthylmethyl)4-(2-Methoxyphenyl)-1,2,4-Triazol-3-Thiol

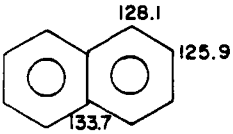
Assignment[a]	Multiplicity[b]	Chemical Shift (ppm)
C-13	s	168.4
C-12	s	154.5
C-2'	s	151.5
C-1	s	133.2
C-9	-	131.4
C-10	-	130.3
[c]C-1'	-	128.8
[c]C-5, [c]C-8	-	128.4
[e]C-6, [e]C-7	-	127.7
[e]C-2	-	126.2
[f]C-3	-	125.7
[f]C-4	-	125.2
C-5'	-	123.6
C-4'	d	120.6
C-6', C-3'	d	112.6
C-14	q	55.6
C-11	t	29.5

[a] Numbering of carbons is shown in the structure 1.

[b] Signal multiplicity obtained from SFORD; s = singlet, d = doublet, t = triplet and q = quartet.

[c,e,f] May be interchanged.

singlet at 133.2 ppm is assigned to C-1. The signals at 131.4, 130.3, 128.4, 127.7, 126.2, 125.7 and 125.2 ppm are assigned to C-9, C-10, both C-5 and C-8, both C-6 and C-7, C-2, C-3, and C-4, respectively. These assignments are in agreement with their calculated values obtained by considering the effect of methyl group on napthalene[11] nucleus 3. Earlier study[12] has reported the chemical shift of 1,2,4-triazole, 4, at 147.6 ppm.



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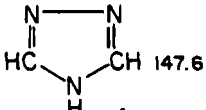

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In 1, C-12 is directly attached to the methylene group while C-13 to a thiol group which is more electronegative as compared to the methylene group. Hence, the remaining two singlets at 168.4 ppm and 154.5 ppm are attributed to C-13 and C-12, respectively.

5-(1-Naphthylmethyl)-4-(2-methoxyphenyl)-1,2,4-triazol-3-yl-thioglycolic acid 2

The chemical shifts of various carbon resonances of 2 are recorded in Table II. The three signals in the upfield region and fifteen signals in the downfield region of the proton noise decoupled spectrum of 2 have been assigned to all the twenty-two carbon resonances. The triplet centered at 29.0 ppm is assigned to C-11 and the quartet centered at 55.6 ppm is assigned to C-14 by comparing the corresponding carbon chemical shifts of 1. The remaining triplet centered at 34.4 ppm is attributed to C-15.

TABLE II

Carbon-13 NMR Chemical Shifts of 5-(1-Naphthylmethyl)-4-(2-Methoxyphenyl)-1,2,4-Triazol-3-yl-Thioglycolic Acid

Assignment[a]	Multiplicity[b]	Chemical Shift (ppm)
C-16, C-13	s	169.4
[c]C-12	s	154.8
[c]C-2'	s	154.4
C-1	s	133.2
C-9	-	131.9
C-10	-	130.1
[e]C-1'	-	128.8
[e]C-5, [e]C-8	-	128.4
[f]C-6, [f]C-7	-	127.4
[f]C-2	-	126.0
[g]C-3	-	125.7
[g]C-4	-	125.1
C-5'	-	123.7
C-4	d	120.9
C-3', C-6'	d	112.6
C-14	q	55.6
C-15	t	34.4
C-11	t	29.0

[a] Numbering of carbons is shown in the structure 2.

[b] Signal multiplicity from SFORD; s = singlet, d = doublet, t = triplet and q = quartet

[c,e,f,g] May be interchanged.

Earlier studies[11] have reported the carbonyl carbon resonances of the carboxylic acids in the range of 165 to 185 ppm. Also, the C-13 signal in **1** is at 168.4 ppm. Hence, the singlet at 169.4 ppm is assigned to both C-13 and C-16. The chemical shifts of remaining carbon resonances have been assigned by comparing the corresponding carbon chemical shifts of **1**.

The hydrogen bonding exists in **1** between the thiol and the methoxy group, but there is no possibility of hydrogen bonding in **2**. Therefore, the carbon resonance of C-2' in **2** is observed at the lowerfield (154.4 ppm) as compared to the corresponding signal of C-2' in **1**.

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REFERENCES

1. T. George, D.V. Mehta, R. Tahilramani, J. David and P.K. Talwalker, J. Med. Chem., 14, 335 (1971).
2. S.S. Parmar, V. Kishore and B. Ali, Agents and Actions, 3, 386 (1973).
3. P.J. Kothari, V. Kishore, V.I. Stenberg and S.S. Parmar, J. Heter. Chem., in press, (1978).
4. S.P. Singh, S.S. Parmar, V.I. Stenberg and S.A. Farnum, Spectroscopy Letters, 11, 59 (1978).

5. S.P. Singh, S.S. Parmar, V.I. Stenberg and S.A. Farnum, ibid, 10, 1001 (1977).

6. S.P. Singh, V.I. Stenberg, S.A. Farnum and S.S. Parmar, ibid, 11, 259 (1978).

7. S.P. Singh, S.S. Parmar and V.I. Stenberg, J. Heterocyclic Chem., 15, 9 (1978).

8. S.P. Singh, S.S. Parmar, V.I. Stenberg and T.K. Akers, ibid, 15, 53 (1978).

9. S.P. Singh, S.S. Parmar, V.I. Stenberg and S.A. Farnum, ibid, 15, 13 (1978).

10. S.P. Singh, S.S. Parmar, V.I. Stenberg and S.A. Farnum, ibid, 15, 541 (1978).

11. G.C. Levy and G.L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley-Interscience, New York, NY, p. 81, 100, 117 (1972).

12. F.J. Weigert and J.D. Roberts, J. Amer. Chem. Soc., 90, 3543 (1968).

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