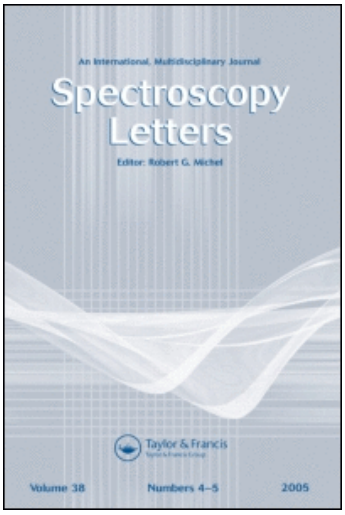

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Carbon-13 NMR of Some New Substituted 2-Amino Benzotheazoles

Salman R. Salman[a]; George Y. Sarkis[b]
[a] Chemistry Department, Faculty of Science, University of Yarmouk, Irbid, Jordan [b] Chemistry Department, College of Science, Al-Mustarsirya University, Baghdad, Iraq

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Carbon-13 NMR OF SOME NEW SUBSTITUTED 2- AMINO BENZOTHEAZOLES .

Salman R. Salman *, Chemistry Department , Faculty of Science, University of Yarmouk , Irbid , Jordan and George Y. Sarkis, Chemistry Department, College of Science, Al-Mustarsirya University, Baghdad, Iraq

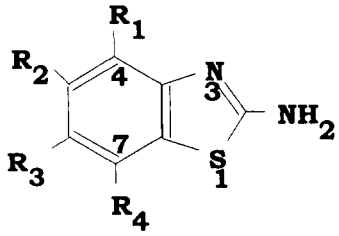
ABSTRACT :

The carbon -13 chemical shift of nine new substituted 2- amino benzothiazole is presented . The calculated chemical shift, using substituent parameters, agrees with the observed one .

INTRODUCTION :

Interest in polysubstituted 2- amino benzothiazoles as potential biologically active compounds have continued because this class of compounds have demonstrated activity as antimalarials, antituberculars, and inflammatory, antinicrobial and anti parasitic (1-8) . A large number of 2-amino thiozole pyridines and 2- amino thiozolequinolines have been synthesized for biological activity work (9) . The IR and ^{1}H NMR spectra of these compounds have

* Author for correspondence



1,R1=R2=R3=R4=H ; 2,R1=R2=R4=H ,R3=F
3,R1=R2=R4=H,R3=Cl ; 4,R1=R2=R4=H,R3=OCH3
5 ,R1=R2=R4=H,R3=OC2H5 ; 6 , R1=R2=R4=H ,R3=N
7,R1=CH3,R2=R4=H,R3=Cl ; 8 , R1=R3=Cl ,R2=R4=H
9,R2=R3=CH3 ,R1=R4=H

[Scheme 1]

shown that they show tautomeric equilibrium . It was though interesting to determine the C-13 NMR chemical
shift for those compounds (Scheme 1) and compare it with the calculated chemical shift .

EXPERIMENTAL :

Synthesis of 2-amino benzothiazole : Bromine (5 mmole) in glacial acetic acid (15 ml) was added slowly during 1.5 hr to a mixture of the amino (p-substituted aniline) (5.9 mmole) and ammonium thiocyanat (12 mmole) in glacial a acetic acid (30 ml) . The reaction mixture was diluted with water and basefied with solid NaOH. The benzothanzole derivative which precipitated was filtered and re crystallized from ethanol . Carbon-13 spectra : The samples were prepared in 5 mm NMR tubes in DMSO- d6 (15-20 % w/v) which was used as a reference . The Carbon -13 NMR spectra were recorded at ambient temperature on a Varian FT80A NMR spectrometer operating at 20MHz . All spectra were width , 45 flip angle , 1s acquisition times 3.5 s delay time .

Table 1 . Experimental and calculated Carbon-13 NMR for substituted 2-Amino-benzothiazole .

	Compound Number								
Shift	1	2	3	4	5	6	7	8	9
δ1,exp	152.89	149.59	151.84	146.95	146.85	158.77	150.69	148.91	152.30
δ1,cal	----	148.39	151.00	146.85	145.85	158.69	151.70	151.40	151.29
δ2,exp	131.26	132.81	132.73	132.20	132.02	131.81	131.89	133.87	130.87
δ2,cal	----	132.66	132.56	132.02	132.36	132.11	132.46	133.86	129.26
δ3,exp	125.84	112.94	124.72	113.39	113.56	122.17	124.45	122.29	127.79
δ3,cal	----	113.00	126.28	113.56	111.44	121.04	123.40	124.38	127.84
δ4,exp	121.24	157.39	125.71	154.78	153.66	141.09	126.18	126.09	122.79
δ4,cal	----	156.04	127.64	153.66	152.64	141.24	127.54	128.94	122.54
δ5,exp	121.24	107.96	120.65	105.93	106.37	117.02	118.05	120.36	130.15
δ5,cal	-----	108.34	121.64	106.37	106.84	116.44	122.34	122.04	128.14
δ6,exp	118.10	118.34	118.73	118.56	118.21	117.78	128.66	125.56	117.62
δ6,cal	----	119.50	119.40	118.21	119.20	119.00	128.30	125.60	118.40
δ7,exp	167.25	166.65*	167.34	165.32	164.91	172.00	166.56	168.99	167.79

* $^{1}J_{CF}$ = 236.4 Hz , $^{2}J_{CCF}$ = 27.12 Hz , $^{3}J_{CCCF}$ = 10.54 Hz

RESULTS AND DISCUSSION :

The Carbon -13 chemical shift of the nine compounds are shown in table 1 . Proton coupled and decoupled carbon-13 spectra were recorded . Calculated chemical shift were based on the additivity rule (10) and substituent induce shifts (11,12) . Table 1 indicates

that , in general , there is a small difference between the calculated and the observed chemical shift . Table 1 give the difference between the calculated and observed chemical shift between the substituted and the unsubstituted C-13 chemical shift for different positions (Δδ) .

Table 2 , Substitution effect on the carbon -13 chemical shift (Δδ) (ppm) of compound 2-9 .

Copd No	Δδ1	Δδ2	Δδ3	Δδ4	Δδ5	Δδ6	Δδ7
2	-3.3	1.5	-12.9	36.2	-13.2	0.2	-0.6
3	-1.1	1.4	-1.1	4.5	-0.5	0.6	0.0
4	-5.9	0.9	-12.4	33.6	-15.3	0.5	2.0
5	-6.0	0.7	-12.2	32.5	-14.5	0.1	-2.4
6	5.9	0.5	-3.6	19.9	-4.2	-0.3	4.7
7	-2.2	0.6	-1.3	5.0	-3.1	10.6	-0.7
8	-4.0	2.6	-3.5	4.9	-0.8	7.5	1.7
9	-0.6	-0.4	2.0	1.6	9.0	-0.5	0.5

$\Delta\delta = \delta$ (substituted) - δ (Unsubstituted) [1]

It is interesting to observe that Δδ for electron donating groups (ie , OCH3 , OC2H5) cause carbon - 1 and carbon - 7 to shift to high field relative to their values in unsubstituted compound , while electron withdrawing group like nitro cause a low field shift to those carbons , relative to their values in compound 1 . It is also interesting to note that the substitution effect has a larger effect on carbon - 2 and 5 . This may be explained on the bases that tautomerism might effect the charge destiny on the sulfur atom more than on the nitrogen atom , and therefore position ipso and para to the sulfur atom are more affected by substitution than carbon - 3 and 6 .

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