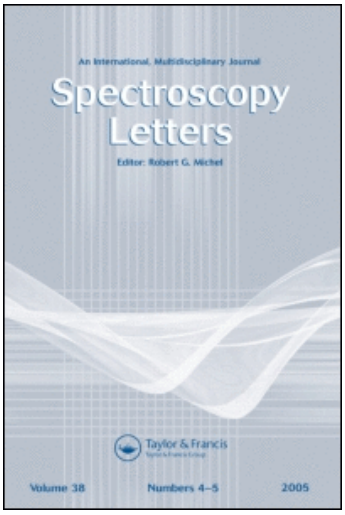

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An Investigation of ^{13}C-NMR Spectra of Some Intramolecular Hydrogen Bonded and Non-Bonded Azo Dyes

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AN INVESTIGATION OF ^{13}C-NMR SPECTRA OF SOME INTRAMOLECULAR HYDROGEN BONDED AND NON-BONDED AZO DYES

Keywords: Substituted azobenzenes, ^{13}C-NMR, Chemical shift assignment, Intramolecular hydrogen bonding, substituted groups.

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ABSTRACT : The ^{13}C-NMR spectra of the azo dyes which were synthesized by reacting substituted benzenediazonium chloride with derivatives of some phenol have been measured. The spectral data of these compounds were described considering intramolecular hydrogen bond and not. The chemical shift assignments were made regarding substituent effects.

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INTRODUCTION

Substituted azobenzenes derivatives have been the most widely used class of dyes due to their versatile features in various fields, such as dyeing textile fiber, bio-medical studies, advanced applications in organic synthesis and high technology areas[1-4]. NMR spectroscopy is an extremely important tool in structural elucidation and in same physical property studies of organic, inorganic and organometalic compounds. It should therefore, not be surprising that NMR spectroscopy may also successfully be used in the analysis of synthetic dyes. Fedorox has summarised ^{13}C NMR results, with the emphasis on azo dyes[5]. The spectroscopic data analysis of azo dyes has been quite difficult and although a few ^{13}C NMR spectra has been described so far, the chemical shift assignment of carbon and the effect of substitued groups reported are very little[6]. The interpretation of the spectra necessitates a correct assignment of the signals in the spectra of the intramolecular hydrogen bonded and non-bonded azo dyes.

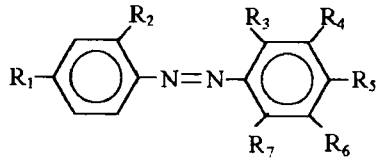
In this study, we report the ^{13}C-NMR chemical shift values of the newly synthesized azo dyes. The influence of the substituents and intramolecular hydrogen bonds on the spectra of the dyes were also described.

EXPERIMENTAL

The dyes 1-13, were prepared by reacting substituted benzene diazonium salts with various phenols as described before [7-9].

The ^{13}C-NMR spectra were recorded on a BRUKER AC 200 Fourier Transform Spectrometer operating at 50.323 MHz. The chemical shift in $CDCl_3$ or DMSO-d_6 as solvent were referenced directly to TMS and reported in ppm to low field of reference. The measurement conditions

TABLE 1. The structures of the azo dyes



	R_1	R_2	R_3	R_4	R_5	R_6	R_7
1	NO_2	H	OH	H	H	s-Bu	H
2	NO_2	Cl	H	H	OH	H	H
3	NO_2	Cl	H	Bu^t	OH	H	H
4	NO_2	Cl	OH	H	H	s-Bu	H
5	H	Cl	H	H	OH	H	H
6	H	Cl	H	CH_3	OH	CH_3	H
7	H	Cl	H	i-pro	OH	H	CH_3
8	H	Cl	OH	H	H	Bu^t	H
9	H	Cl	OH	Bu^t	H	CH_3	H
10	H	H	H	H	OH	H	H
11	H	H	H	CH_3	OH	CH_3	H
12	H	H	OH	H	H	Bu^t	H
13	H	H	OH	Bu^t	H	OCH_3	H

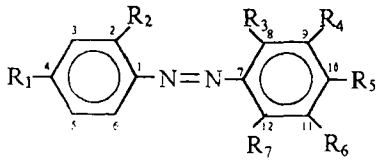
i-pro : izo-propyl s-Bu : Sec-butyl

were as follows : pulse with (pw) : 2 μs; acquisition time (AQ) : 2.621 s for 128 K data table with a spectral width (sw) of 250 ppm. Spectra were recorded with broad-bond decoupling and a digital resolutions of 0.381 Hz/pt.

RESULTS AND DISCUSSION

The azo dyes synthesized and the ^{13}C chemical shift data of them are shown in Table I and II, respectively of which the results of the dyes 10, and 12 have already published before[9] and included here the discussion by comparing with the other dyes.

TABLE 2. The ^{13}C-NMR data of the dyes



No	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12
1*	150.97	122.00	125.02	148.33	125.02	122.00	137.48	153.94	118.08	134.34	139.68	131.66
2**	151.85	118.56	125.77	147.86	123.46	133.12	145.86	126.27	116.40	163.02	116.40	126.27
3**	151.94	118.56	125.80	147.73	123.28	133.00	145.70	123.46	136.69	161.88	117.16	123.96
4*	150.08	118.54	125.94	148.24	122.71	133.72	138.23	151.63	117.81	135.27	139.86	132.03
5*	148.70	117.60	131.10	134.50	130.67	127.30	147.18	125.56	115.92	158.88	115.92	125.56
6**	148.27	117.49	131.38	133.11	130.56	127.93	145.32	125.06	123.70	157.69	123.70	125.06
7**	148.53	117.72	130.99	133.23	130.44	127.86	143.52	116.68	132.94	159.13	113.90	138.73
8**	146.46	117.59	132.08	133.08	130.56	128.19	137.52	151.26	117.98	132.56	142.53	124.16
9*	146.48	117.35	131.35	133.60	130.42	127.91	137.77	150.64	138.63	127.47	132.69	131.25
10**	152.16	122.17	129.22	130.36	129.22	122.17	145.34	124.93	115.97	161.05	115.97	124.93
11*	152.21	122.38	129.04	130.27	129.04	122.38	128.26	124.13	123.93	155.11	123.93	124.13
12*	150.68	122.15	129.32	130.87	129.32	122.15	136.89	150.40	117.67	130.95	142.88	129.71
13*	151.99	121.97	129.33	130.66	129.33	121.97	137.00	150.37	140.11	110.57	148.20	120.72

* $CDCl_3$ **DMSO-d6

TABLE 3. The ^{13}C-NMR data of substitued groups

No	Group	C-13	C-14	C-15	C-16
1	R_6 : $CH_3CHCH_2CH_3$	21.61	40.44	30.95	12.00
3	R_4 : $C(CH_3)_3$	34.46	29.05	-	-
4	R_6 : $CH_3CHCH_2CH_3$	21.54	40.46	30.94	12.00
6	R_4 and R_6 : CH_3	16.70	-	-	-
7	R_4 and R_7 : CH_3CHCH_3 , CH_3	22.21	26.45	22.21	16.89
8	R_6 : $C(CH_3)_3$	33.83	31.01	-	-
9	R_4 and R_6 : $C(CH_3)_3$, CH_3	35.08	29.45	20.63	-
11	R_4 and R_6 : CH_3	16.05	-	-	-
12	R_6 : $C(CH_3)_3$	34.12	31.38	-	-
13	R_4 and R_6 : $C(CH_3)_3$, OCH_3	35.24	29.44	55.75	-

Considering all dyes synthesized, it is clearly seen that ortho-hydroxyazobenzene derivatives 1, 4, 8, 9, 12, and 13 contain intramolecular hydrogen bonds and exist in the azo form, in addition para-hydroxyazobenzene derivatives 2, 3, 5, 6, 7, 10, and 11 exist exclusively in the azo form and do not form any intramolecular hydrogen bond[10-12]. The signals of C-8 atoms of the dyes 1, 4, 8, 9, 12, and 13 containing intramolecular hydrogen bond, have the effect of deshielding relative to the other dyes 2, 3, 5, 6, 7, 10, 11 and deshield approximately by 25 ppm (Table II). As can be observed from the values of C-10 atoms of the dyes 2, 3, 5, 6, 7, 10, and 11 which have para-hydroxyl groups , that the chemical shift values are between 155.11 ppm and 163.02 ppm, and it is in their region of 135.27 ppm and 110.57 ppm for the other dyes depending on the chemical environment of the carbon[10]. When the chemical shift values of C-1 atoms attached to nitrogen are between 148.27 ppm and 152.21 ppm, the signals of C-7 atoms attached to the other nitrogen appear at 128.26-147.18 ppm.

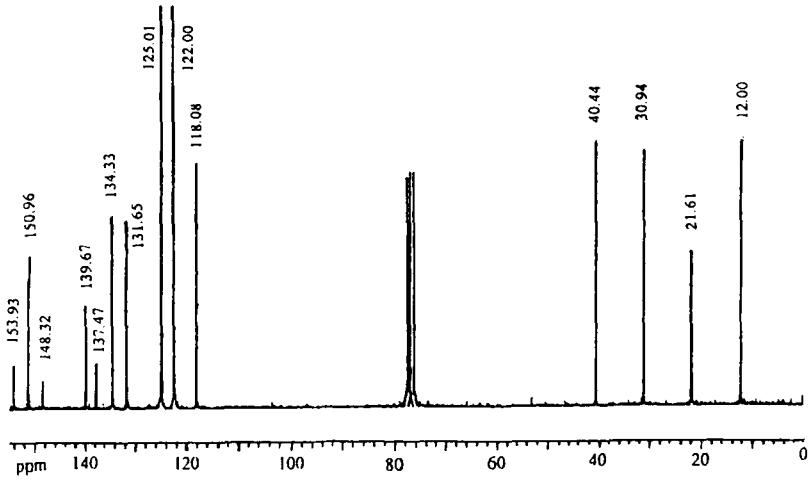


Figure 1. The ^{13}C-NMR spectrum of the dye, 1

In investigating the dyes of aniline, 2-chloroaniline, and 2-chloro-4-nitroaniline derivatives, a harmonious in the chemical shift values of C-1, C-2, C-3, C-4, C-5, and C-6 atoms for the dyes of derivatives of each series has been detected. For instance, looking at the chemical shift values of C-1, C-2, C-3, C-4, C-5, and C-6 atoms of the dyes 10, 11, 12, and 13 (Table II), close similarities among all the values are obvious. This is also the case for the dyes 5, 6, 7, 8, and 9 which are the derivatives of 2-chloroaniline. Chemical shift values in the range 122.38 ppm and 121.97 ppm from attaching chloride to C-2 atom of aniline derivatives were shielded downward to the 117.72 ppm- 117.35 ppm internal. Attaching the nitro group to C-4 atom of the 2-chloroaniline shielded by 1 ppm like the dyes 2, 3, and 4. As can be seen the dyes 1,2,3, and 4 having nitro groups, C-4 atoms were deshielded by aproximately 17 ppm and 15 ppm relative to the aniline and 2-chloroaniline derivatives , respectively. In

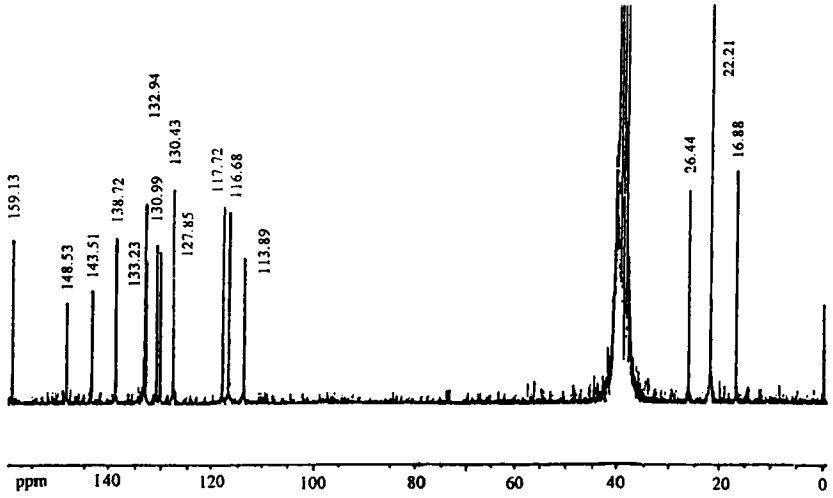


Figure 2. The ^{13}C-NMR spectrum of the dye, 7

examining the dyes groups like 2, 5, 10 or 1, 4 or 6, 11 or 8, 12 being analogous to phenol derivatives, there seems them to have similar values of C-7, C-8, C-9, C-10, C-11, and C-12. Figures I and II show the ^{13}C-NMR spectra of the dyes 1 and 7, respectively one of which is intramolecular hydrogen bonded and the other non-bonded.

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