

## <sup>13</sup>C NMR Investigation of Some New Azodiamines

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Three new organic compounds viz., 2,2'-dimethyl-4,4'-diaminoazobenzene, 2,2'-dichloro-4,4'-diaminoazobenzene and 2,2'-dimethoxy-4,4'-diaminoazobenzene have been synthesised and their structures confirmed by <sup>1</sup>H and <sup>13</sup>C NMR data with selective <sup>13</sup>C-<sup>1</sup>H decoupling along with other spectral data. The chemical shifts of C-1 to C-6 carbons of the phenyl group were correlated with the substituent effects.

**Key Words:** Azodiamines, <sup>13</sup>C NMR, Substituent effect.

### INTRODUCTION

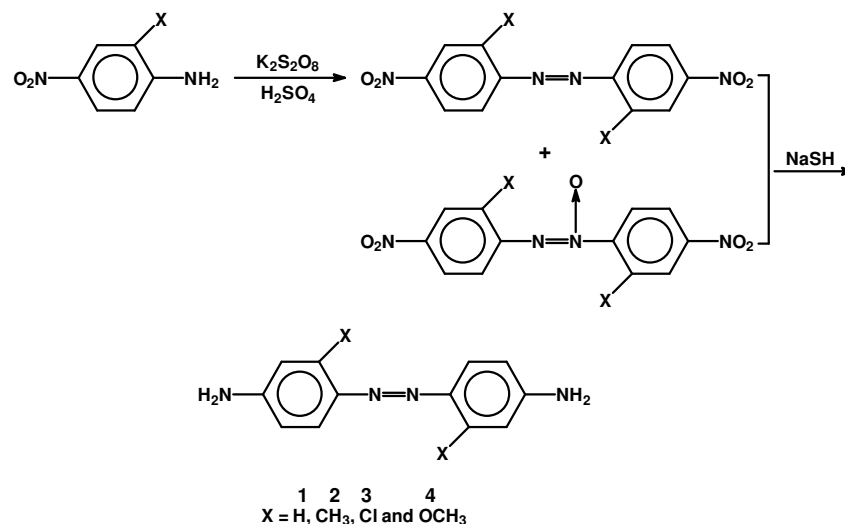
<sup>13</sup>C NMR chemical shift measurements of benzene derivatives<sup>1</sup> are increasingly used as probe for the investigation of electronic effects of the substituents and their mode of transmission through aromatic and other unsaturated systems. The effect of substituents in the ring on the chemical shifts of carbon is of obvious interest especially in those cases where the side chain is conjugated with another ring. This allows resonance interaction with *para* substituents to take place and the effect of distance on the extent of such interactions can be explored. In addition, for the case of *ortho* substituents, the variation of substituent induced chemical shift with steric effect also plays important role in the determination of structure<sup>1</sup>. This paper reports the <sup>1</sup>H and <sup>13</sup>C NMR studies on three new aromatic diamines synthesized viz., 2,2'-dimethyl-4,4'-diaminoazobenzene, 2,2'-dichloro-4,4'-diaminoazobenzene and 2,2'-dimethoxy-4,4'-diaminoazobenzene.

### EXPERIMENTAL

From the reaction products of 2-substituted-4-nitroaniline with aqueous K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/H<sub>2</sub>SO<sub>4</sub>, leading mainly to 2,2'-disubstituted-4,4'-diaminoazobenzene, three new organic compounds (**2**, **3** and **4**) have been isolated<sup>2</sup>.

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The NMR spectra were measured at 90 MHz ( $^1\text{H}$ ) with EM-390 spectrometer and 50.33 MHz ( $^{13}\text{C}$ ) with XL-200 spectrometer using 5 mm 0. d sample tubes. Probe temperature was 20 °C and conc. used was 0.25 mol  $\text{L}^{-1}$ .  $\text{D}_2\text{O}$  in a 1 mm o.d capillary was used as an external lock substance for recording  $^{13}\text{C}$  spectra. TMS was also used as an internal reference of both the  $^1\text{H}$  and  $^{13}\text{C}$  shifts. The spectra were recorded in the CW frequency sweep mode at about 25 °C.

## RESULTS AND DISCUSSION

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR chemical shifts ( $\delta$ ) of compounds **2-4** are given in Table-1.

The spin multiplicities (d-doublet, t-triplet) determined by off-resonance  $^{13}\text{C}$ - $^1\text{H}$  proton decoupling are also shown.  $^{13}\text{C}$  NMR spectrum of 2,2'-dimethoxy-4,4'-diaminoazobenzene revealed that this compound consists of 7 magnetically non-equivalent carbon atoms and 5 non-equivalent hydrogen atoms. The C-1, C-2 and C-4 are the carbon atoms which do not have any proton.

$^{13}\text{C}$  resonances of all the substituted diamines were assigned to the respective carbon based on long-range  $^1\text{H}$  coupling patterns. The observation that the peak at 157.8 ppm of  $\text{CH}_3\text{O}$ -substituted diamine as a long-range doublet ( $J = 5.0$  Hz) confirms that the carbon containing the  $\text{NH}_2$  group 'sees' only one *m*-proton. This puts the  $-\text{OCH}_3$  group at the C-2 position. Hansen and his co-workers have calculated  $^{13}\text{C}$ - $^{13}\text{C}$  coupling constants and give the correct order as

$$^1J_{\text{CH}} \gg ^3J_{\text{CH}} > ^2J_{\text{CH}} > ^4J_{\text{CH}} \text{ (along with the correct signs).}$$

Usually one does not observe  $^2J_{\text{CH}}$  (in the order 1-2 Hz). The peak at 133.4 ppm is a triplet with two *meta*-protons (thus assigned to  $\text{C}_1$ ) and the

TABLE-1  
<sup>1</sup>H NMR AND <sup>13</sup>C NMR PARAMETERS OF COMPOUNDS 2, 3 AND 4  
 (δ IN ppm FROM TMS, J IN Hz)

Chemical shifts/ coupling constant	2	3	4	X	Y
δH-3	5.6(s)	6.1 (s)	5.5 (s)	-0.5	0.5
a δH-5	6.4(d)	6.7 (d)	6.4 (d)	-0.3	0.3
b δH-6	7.5 (d)	7.5 (d)	7.4 (d)	0.0	0.1
δNH <sub>2</sub>	3.3 (s)	3.4 (s)	3.8 (d)	-0.1	-0.4
N-H					
CH <sub>3</sub>	2.4 (s)	-	3.35 (s)	-	-
δC-H					
δC-1	141.787	138.330	133.429	3.457	4.901
δC-2	138.390	135.782	152.158	2.608	-16.376
δC-3	114.479	112.925	106.278	1.554	6.647
δC-4	150.370	152.147	157.812	-1.777	-5.665
δC-5	112.047	111.195	97.006	1.852	15.849
δC-6	116.649	118.447	117.366	-1.798	-1.081
δC-7	17.579	-	55.420	-	-
<sup>1</sup> J (C-3, H-3)	94.3	d	159.0	-	-
<sup>1</sup> J (C-5, H-5)	121.5	d	156.0	-	-
<sup>1</sup> J (C-6, H-6)	108.2	161.9	158.8	-53.7	3.1
<sup>1</sup> J (C-7, H-7)	128.1	-	144.2	-	-
<sup>2</sup> J (H-7, H-7)	4.9	-	c	-	-
<sup>2</sup> J (C-6, H-5)	2.6	-	-	-	-
<sup>3</sup> J (C-1, H-3)	d	6.6	5.0	-	-
<sup>3</sup> J (C-1, H-5)	d	6.1	5.0	-	-
<sup>3</sup> J (C-2, H-6)	5.7	9.7	11.1	-4.0	1.4
<sup>3</sup> J (C-3, H-5)	6.3	d	5.3	-	-
<sup>3</sup> J (C-4, H-6)	9.6	10.5	5.0	-0.9	5.5
<sup>3</sup> J (C-5, H-3)	5.3	d	8.0	-	-

a and b = Signals assigned basing Sadtler Handbook of <sup>1</sup>H NMR spectra.

c = This coupling is not observed because the exchange rate of H-7 is high on the NMR time scale.

d = Not observed.

peak at 152.2 ppm is C-2 (doublet with one *meta*-proton). The signal at 117.4 ppm is assigned to C-6 because it shows only <sup>1</sup>J<sub>CH</sub> and no observable <sup>3</sup>J<sub>CH</sub>. C-6 is the only carbon without any *meta*-proton. The assignment of C-3 and C-6 to the peaks at 106.3 and 97.0 ppm, respectively is obvious and if fits the positions (*ortho* to NH<sub>2</sub> is shielding effect with respect to benzene chemical shift). In order to confirm the validity of present assignments, an attempt was also made to theoretically calculate the chemical shifts. The substituent chemical shifts<sup>3</sup> were added to the <sup>13</sup>C chemical shifts of *trans*-

azobenzene (DMSO- $d_6$ )<sup>4</sup> at 300 K. The agreement between the calculated and observed chemical shifts is seen to be fairly good (Table-2). The correctness of the assignment was also verified from the multiplicity of the signals in the proton coupled spectrum.

TABLE-2  
<sup>13</sup>C CHEMICAL SHIFTS AND SUBSTITUENT  
 PARAMETERS OF COMPOUNDS 1 TO 4

Compd.	R1	R2	X	$\sigma_1$	$\sigma_2$	$-E_s^*$	Calcd. (obs.)					
							C-1	C-2	C-3	C-4	C-5	C-6
1	NH <sub>2</sub>	NH <sub>2</sub>	H	0.00	0.00	0.00	139.4 (136.0)	123.0 (117.0)	115.1 (116.5)	152.1 (148.0)	152.1 (116.5)	123.0 (117.0)
2	NH <sub>2</sub>	NH <sub>2</sub>	CH <sub>3</sub>	-0.05	-0.10	1.24	136.4 (141.8)	132.0 (138.4)	115.7 (114.5)	152.0 (150.4)	- (112.1)	- (116.7)
3	NH <sub>2</sub>	NH <sub>2</sub>	Cl	0.51	-0.20	0.97	138.2 (138.3)	127.9 (135.8)	115.2 (112.9)	154.1 (152.2)	- (111.2)	- (118.5)
4	NH <sub>2</sub>	NH <sub>2</sub>	OCH <sub>3</sub>	0.25	-0.41	0.55	131.5 (133.4)	154.0 (152.2)	100.7 (106.3)	153.3 (157.8)	- (97.0)	- (117.4)

\*Negative sign implies that the group X is larger than the reference H atom.

A careful analysis of the Table-1 shows that interestingly only in methyl substituted diamine, C-1 is not coupled with H-3 or H-5. Except for <sup>1</sup>J (C-6, H-6) and <sup>3</sup>J (C-2, H-6) which are sufficiently modified by the introduction of chlorine or methoxy substituents, the couplings do not change, thus confirming the structural similarity of the three diamines. The chemical difference between C-2 and C-6 lies principally in the extent of their interaction with the lone pairs on the distant nitrogens. It is evident that C-6 is not at all affected by substituent (Table-2). As expected, C-2 and C-5 (*p*-carbon to the substituents X) have the most shifted signals compared to 4,4'-diaminoazobenzene (**1**) with a positive  $\alpha$ -effect and a negative  $\beta$ -effect, respectively. Both azobenzene and its *ortho* substituted homologues are almost certainly non-planar<sup>5</sup>. Hence, it is possible to assign the non-planar structures for the three azodiamines of our discussion. The non-planar structures are favoured because they reduce repulsion between the *ortho* substituents of azobenzene and the distant nitrogen lone pairs. This view is supported by the <sup>13</sup>C NMR spectra (Table-1). The effect of the substituent size (group radii of CH<sub>3</sub> 1.73, of OCH<sub>3</sub> 1.95 and atomic radii of Cl 1.89) can be inferred from the difference in chemical shift values X and Y. There is little variation of the chemical shift of C-1 with substituent size. We interpret this as evidence that the C-N=N-C geometry (*i.e.*, the hybridization of the nitrogen atoms) is unaffected by substitution. Again as expected, the effect of the OCH<sub>3</sub>

group is more because of its bulkiness. The C-2 of methyl substituted diamine shows highest multiplicity due to interaction with the protons of methyl group.

The theoretical calculation of chemical shifts of C-5 and C-6 in these systems is rather difficult, it would be desirable to make empirical correlations to make chemical shift predictions and to test assignments. Such a correlation should use a minimum set of parameters (like  $\sigma$ , R, Q and I) and should reflect or current understanding of the relationship between molecular structure and molecular properties. An attempt was, therefore, made to correlate the observed <sup>13</sup>C NMR chemical shifts of these poly-substituted aromatic compounds with inductive, resonance and steric parameters<sup>6</sup>. First observation is that the inductive effects of the substituents have a linear variation on the chemical shift of C-6, the *m*-carbon (Fig. 1). The other *meta* carbon (C-4) is randomly influenced by the substituents since NH<sub>2</sub> group which is attached at C-4 position 'sees' only the adjacent proton H-3. Secondly, greater the electron-attracting power of a substituent, higher is the downfield shift. Further, the substituents do not have any appreciable effect on the *ortho* positions or on C-2.

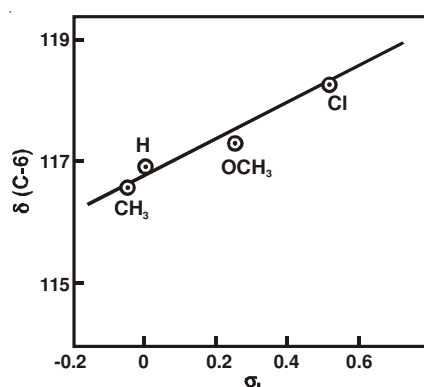


Fig. 1. Relationship between the chemical shift at C-6 and inductive parameters  $\sigma_I$  for compounds 1-4

Since  $\sigma_R^\circ$  is a substituent constant reflecting the resonance interaction of the substituent with the ring, it is interesting  $\sigma_R^\circ$  correlates well with the chemical shift of C-3 and C-4 but slight deviation is observed in C-5 (Fig. 2). This may be due to the higher electronegativity of chlorine atom that affect the resonance interaction at the *para* carbon. Trends for other ring sites are rather less clear<sup>7</sup>. As expected steric substituent constant  $E_s$  fits well with the chemical shifts of C-1 and C-4 (Fig. 3). Hydrogen atom does not fall in line along with the substituents since no interaction occurs between H-1 and lone pair of electrons on nitrogen atoms of azo group. It can be observed

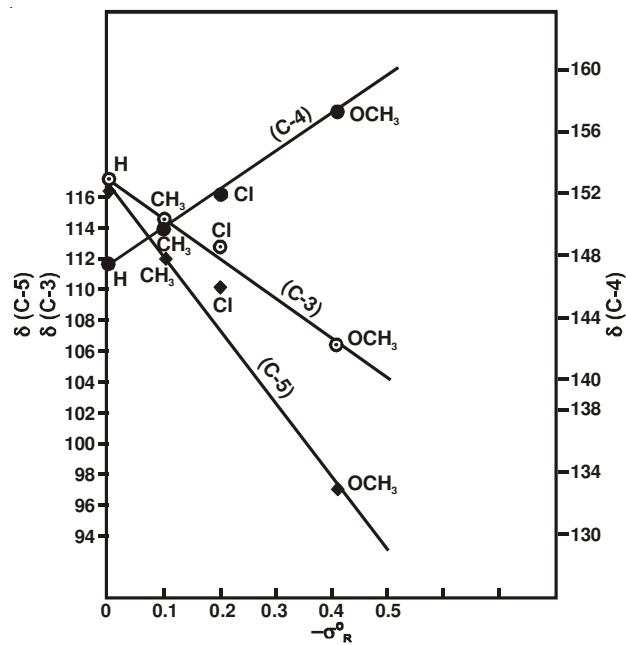


Fig. 2. Relationship between the chemical shift at C-3, C-4 and C-5, and the resonance parameter  $\sigma_R^o$  for compounds **1-4**

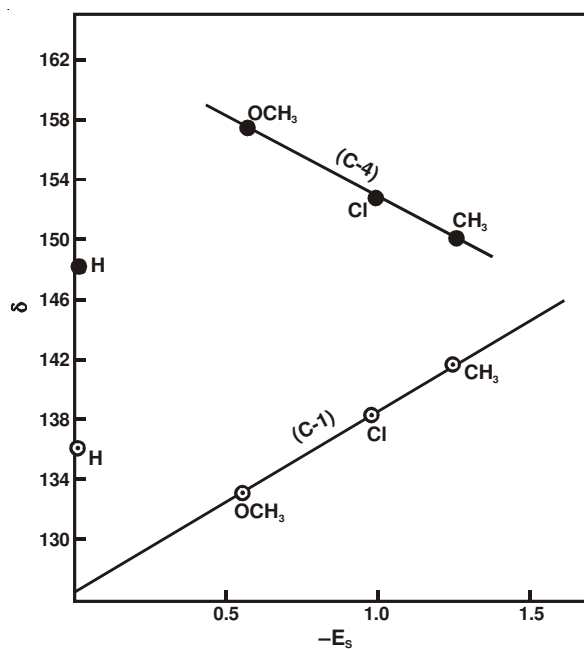


Fig. 3. Relationship between the chemical shift at C-1 and C-4, and the steric substituent parameter  $-E_s$  for compounds **1-4**

that when the size of the substituent is increased, a shift of C-1 to higher field is observed whereas an opposite effect is noted for C-4. This may be due to the higher shielding effect of the bulky substituents on the chemical shifts of C-1 carbon atom. A deshielding effect is, therefore, to be observed on the substituent induced chemical shifts of C-4. Also, the shieldings effect has its influence on the chemical shifts of C-5 which seem to vary widely and hence not comparable.

### REFERENCES

1. M. Godfrey, *J. Chem. Soc., Perkin Trans.*, 2769 (1977).
2. O.N. Witt and E. Kopetschi, *Ber.*, **45**, 1136 (1912).
3. D.F. Ewing, *Org. Mag. Res.*, **12**, 499 (1979).
4. A. Lycka and Dobroslav, *Org. Mag. Res.*, **15**, 391 (1981).
5. C.L. Forber, E.C. Kelusky, N.J. Bunce and M.C. Zerner, *J. Am. Chem. Soc.*, **107**, 5884 (1985).
6. O. Exner, Advance in Linear Free Energy Relationship, in: A Review of the Hammett Equation, Ch. 1 (1972).
7. N. Inamoto, S. Masuda, K. Tokumaru, K. Tori, M. Yoshida and Y. Yoshimura, *Tetrahedron Lett.*, **17**, 3707 (1976).

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